

INDIAN JOURNAL OF PHYSICS

VOL. XII

AND

PROCEEDINGS

OF THE

Indian Association for the Cultivation of Science, Vol. XXI.

(Published in Collaboration with the Indian Physical Society)

BOARD OF EDITORS

D. M. BOSE, PH.D. K. PROSAD, M.A. S. K. MITRA, D.Sc.

P. N. GHOSH, PH.D., *Secretary.*

(With Eleven Plates)

PRINTED AT THE CALCUTTA UNIVERSITY PRESS, SENATE HOUSE, CALCUTTA,
BY BHUPENDRALAL BANERJEE AND PUBLISHED BY THE SECRETARY,
INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,

210, Bowbazar Street, Calcutta.

1938.

Price Rs. 12 or £1-2-6.

SUBJECT INDEX

	PAGE
Absorption in Ionised Gas, The Theory of, I. Opacity in Stellar Material. II	
Optical Properties of Liquid Metals—By Bibha Majumdar	233
Attenuation of Ultra Short Radio Waves along the Earth, The—By S. R.	
Khashtgi and M. K. Chakravarty	289
Cathodic Sputtering—By U. K. Bose	95
Chladni Figures, On the Excitation of—By L. Sibaiya	407
Cosmic Ray Showers—Hard—By W. Bothe	155
Dielectric Properties of some Organic Substances—By G. R. Paranjpe and	
D. J. Davari	283
Earth's Atmosphere—On the Intensity of Ionisation in the—By A. C.	
Banerji and P. L. Bhatnagar	387
Electric Conduction due to α Electrons in some Trivalent Rare Earth	
Compounds, On the—By Krishnapada Ghosh and Bonbchari Ghosh	259
Electrical Constants of Soil and Radio Frequencies, Effect of Temperature	
on the—By R. D. Joshi	1
Heat Capacities of a few Crystals at Low Temperatures, On the—By S. C.	
Sirkar and J. Gupta	145
Interchange of Electricity between Solids, Liquids and Gases in Mechanical	
Action, On the—By S. K. Banerji	409
Ionised Gas—See Absorption	
<i>Ionosphere:—</i>	
On the Total Reflection of Electromagnetic Waves in the Ionosphere—By	
S. N. Bose	121
A Study of the F Region of the Ionosphere—By R. R. Bajpai and B. D.	
Pant	211
Dispersion, Absorption and Polarisation Curves for Radio Wave Propagation	
in the Ionosphere—By Sarajuprasad Ghosh	341
Stratification of the Ionosphere—By J. N. Bhar	363
The Lower Ionosphere—By S. K. Mitra, J. N. Bhar and S. P. Ghosh	455
Light Scattered by Binary Mixtures—on Anomalous Depolarisation of—	
By Birendrakrishna Mookerjee	15
Liquids, On the Theory of—By A. Ganguli	25
Magneto Resistance Change of Ferro-Magnetics in the Alternating Magnetic	
Field—By S. Sharan	203
Non-Partial Differential Equation of the Elliptic Parabolic Type, On the	
Theory of a—By M. Raziuddin Siddiqi	109
Oscillator Determination of the Frequency of an, with a Condenser—By	

	PAGE
Pianoforte String and the Hammer, Dynamics of the, Part I (Hard Hammer)	
—By Mohinimohan Ghosh	317
Pianoforte String and the Hammer, Dynamics of the, Part II—By Mohini-	
mohan Ghosh	437
<i>Raman Spectra :—</i>	
Raman Effect in Boric Acid and some Boron Compounds—By S. M.	
Mitra	
On the Origin of New Raman Lines due to Molecules in the Solid State	
and the Wing due to Liquids—By S. C. Sirkar and J. Gupta ...	35
The Constitution of Heavy Water—By I. Ramakrishna Rao and P.	
Koteswaram... ..	63
Hexa Co-ordination in Telluric Acid and in Molybdates and Tungstates in	
Solution—By Jagannath Gupta	223
On the Raman Spectra of Diphenyl—By S. K. Mukerji and S. Abdul	
Aziz	271
Dissociation in Sulphuric Acid with Temperature—By P. Koteswaram ...	299
Origin of Low Frequency Raman Lines in Solids—By Jagannath Gupta ...	355
<i>Spectra :—</i>	
On the Hyperfine Structure and Analysis of some Complex Lines in the	
First Spark Spectrum of Arsenic in the Ultra-Violet Region—By S. K.	
Mukerji	331
The Spectrum of Argon IV—By A. Balankeswara Rao	399
<i>Upper Atmosphere :—</i>	
Distribution of Constituent Gases and their Pressure in the Upper Atmos-	
phere—By S. K. Mitra and H. Rakshit	47
The Theory of Molecular Dissociation and the Fundamental Mechanism in	
Upper Atmosphere—By R. C. Majumdar	75
<i>X-rays and Crystal Structure :—</i>	
Structure of Aromatic Compounds Part III : Benzophenone—By K.	
Banerjee and A. Haque	87
A Study of Sulphur Allotropes by the X-ray Diffraction Method, Part I.—	
By S. R. Das	163
Space Group of Creatinine—By K. Banerjee and Abdul Haque ...	183
Space Group and Atomic Arrangement in Phloroglucine Dihydrate—By	
K. Banerjee and Rajiuddin Ahmed	249
Thermal Co-efficient of Rocksalt by X-ray Reflection—By Sudhendu Basu	
and A. T. Maitra	305

EFFECT OF TEMPERATURE ON THE ELECTRICAL CONSTANTS OF SOIL AT RADIO FREQUENCIES.*

By R. D. JOSHI, M.Sc., Assoc., I.R.E.

University Research Scholar, Benares Hindu University.

(Received for publication, January 13, 1938.)

ABSTRACT Variation of dielectric constant and conductivity of soil with temperature from 0°C to 105°C at high radio frequencies have been determined by substitution method by measuring the capacitance and resistance of a condenser with dry soil as dielectric. The conductivity was found to be of the order of 3.4×10^{-5} e.s.u. at 0°C and 8.2×10^{-5} at 105°C . The value of the dielectric constant was found to be about 4.0 and it remained fairly constant with rise of temperature. The temperature coefficient of conductivity is found to be positive and the value is 2.0 per cent. per degree centigrade at 20°C and it increases with the frequency. It has been concluded from these observations and also from some previous results that the value of conductivity of soil will be higher in summer and rainy season than in winter.

INTRODUCTION

The knowledge of the electrical constants of soil at high frequencies has been found to be of considerable importance in Radio Engineering as they are the chief elements in determining the effective 'service area' of a Broadcasting Station. Consequently, these constants of the soil and also the effects of moisture, temperature and frequency on these have been recently determined by various workers.^{1,2,3,4,5} The electrical properties of Indian soil at various radio frequencies and at various moisture contents have been studied by Khastgir and Sengupta⁶ and lately by us.^{7,8} It has been shown that the conductivity and dielectric constant considerably increase with moisture content present in the soil. Besides the moisture, the temperature also has a marked influence on the electrical constants of soil. A short account of the work of a few early investigations on this will be given below.

Hopkinson⁹ was one of the earliest investigators to show clearly that the absorption in a dielectric increases with temperature. The only considerable attempt to account for the influence of temperature from a theoretical standpoint was that of Wagner.¹⁰ Proceeding from Maxwell's theory of layer dielectric, and observations on a paper condenser, he concluded that the effect of temperature was to increase the rate of decay. Whitehead¹¹ found that the

* Communicated by the Indian Physical Society.

influence of temperature was mainly in the variation of the conductivity and not the dielectric constant which changed by only a small amount as the temperature was increased.

The effect of temperature on the conductivity of soil was studied experimentally by Higgs.¹² He found by the direct measurement with the alternating current of a frequency of 50 cycles per second that the conductivity was of the order of 7.5×10^7 c.s.u. The variation between -15°C . to 20°C . showed that the conductivity increased with temperature, and the temperature coefficient of conductivity was found to be about 3% per $^\circ\text{C}$. Smith-Rose⁵ has also shown the above change of conductivity at a frequency of 1200 kc. per second. He measured the variation from -3°C to 30°C . The conductivity in his case was found to be of the order of 10^8 c.s.u. and the temperature coefficient of conductivity was 2.5% per $^\circ\text{C}$. The conductivity and dielectric constant were found to drop suddenly near 0°C . It will be evident from the above investigations that the temperature has a marked influence on the electrical constants of soil. The effect of temperature on the electrical constants of soil should therefore specially be found in the tropical countries where there are many places the temperatures of which vary within fairly wide limits in different seasons of the year. In view of this, the effect of temperature on these constants have been studied by us, the results of which are recorded in the present communication.

THEORY

The theory of the method consists in finding the effective capacitance and conductance of a condenser with soil as the dielectric. In the early investigations mentioned in the introduction the method of reactance variation was mostly applied to find the conductance. This method, however, suffers from the defect that the current following in the tuned circuit cannot be made very high as then it will react appreciably on the oscillator circuit which is assumed to be constant. Moreover, for finding out the effect of temperature the method is not suitably applicable as the temperature of the soil hardly remains constant continuously for a considerably long time required for one complete observation. To avoid the above difficulties the substitution method has been adopted in the present work. In this method the soil condenser is connected for a very small period as required to tune the circuit to resonance and then it is disconnected. For the small time required for observation the temperature of soil remains fairly constant. A simple analysis of the process is given below.

Let A be the area of the condenser plates in sq. cm. and d the distance between them in cm. If the distance between the plates be filled with the soil of conductivity σ , the resistance of the condenser with soil as the dielectric, will

be given by

$$R_s = d / \sigma A$$

$$= \frac{1}{4\pi\sigma} \times \frac{4\pi d}{A}$$

$$= \frac{9 \times 10^{11}}{4\pi\sigma C_a} \text{ in c.s.u.}$$

If R_s be measured in ohms, as has been done in the present experiment, the conductivity will be given by,

$$\sigma = \frac{9 \times 10^{11} \times 9}{4\pi C_a R_s}$$

The dielectric constant of soil will be given as usual by $K = C_s / C_a$.

where C_a = the capacitance in $\mu\mu$ F of the condenser with air as the dielectric,

C_s = the capacitance in $\mu\mu$ F of the condenser with soil as the dielectric,

σ = conductivity of soil in c.s.u.

EXPERIMENTAL ARRANGEMENT AND OBSERVATIONS

The condenser for finding out the electrical constants of soil at high frequencies consisted of two parallel metal discs of 5.5 cm. diameter which were placed a few centimetres apart. This condenser with soil as the dielectric was kept in an air-tight glass tube B, shown in figure 1, which could be heated uniformly by an electric heater. The temperature of the soil could be determined by the thermometer T. A resonant circuit (L-C) was coupled to a valve generator (H. F. O. Fig. 1) emitting waves of the desired frequencies. A double pole double throw switch (S) connected the resonant circuit either to the soil condenser or to a variable non-inductive high resistance R. A Moullin's thermionic voltmeter (T. V.) was connected across the variable condenser to observe the resonance point. The resonant circuit (L, C) was tuned to resonance and the plate condenser in the glass tube with air as dielectric was then connected in parallel with the tuning condenser C and the circuit retuned. The decrease in the value of C at resonance gave C_a . The process was repeated with soil between the plates of the condenser and the value of C_s was thus obtained.

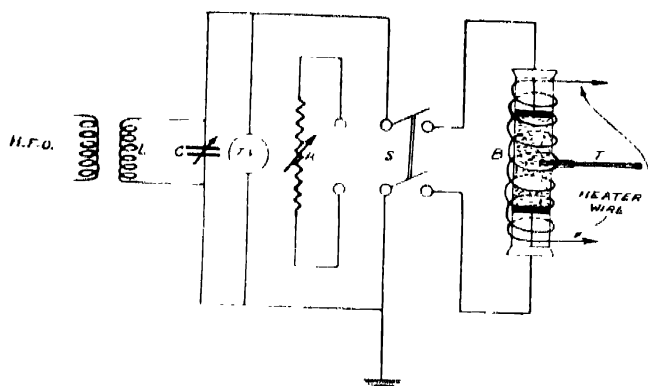


FIGURE 1.

To measure the conductance of the soil the circuit was tuned to resonance with the unknown reactance of the soil condenser in the circuit and the reading of the thermionic voltmeter taken. The switch was then thrown to the variable resistance R , the circuit retuned, and R adjusted to give the same voltmeter reading as found in the previous case when the soil was in the circuit. The value of R was then equal to R_s , the resistance of the soil condenser. To find the constant at 0°C the tube B was immersed in ice and perfectly sealed so that no moisture could penetrate inside it. A special care was taken to remove all the

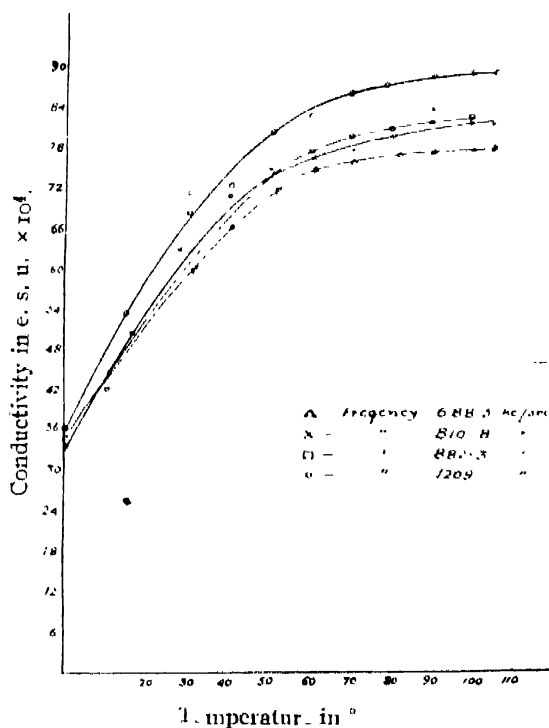


FIGURE 2.

moisture from the soil before determining its constants, as the condenser with moist soil between the plates would behave like an electrolytic condenser, the capacity of which rises with temperature. Thus the true change of the capacity due to change in the constants of the soil as dielectric would not be obtained with moist soil. The values of the electrical constants of the soil were determined at different frequencies in the broadcast band.

The curves in figure 2 show the variation of conductivity of the soil with temperature at different frequencies. There was no perceptible change observed in the values of dielectric constant as the temperature was increased.

The four tables below contain the values of the dielectric constant and conductivity of the soil at different temperatures for the four frequencies observed. The second column in each table gives the values of the substituted resistance observed experimentally.

TABLE I.

Frequency 1200 Kc/Sec.

Temperature in degrees centigrade	Resistance (R _s) in ohms.	Dielectric constant (K)	Conductivity (σ) in e. s. u.
0	87,500	4.1	3.603×10^5
15	88,500	4.0	5.389×10^5
30	44,000	4.2	7.161×10^5
40	13,500	4.0	7.247×10^5
50	39,000	3.8	8.683×10^5
60	38,000	3.8	8.206×10^5
70	37,500	3.8	8.409×10^5
80	36,900	3.9	8.758×10^5
90	35,500	3.8	8.882×10^5
100	35,250	4.0	8.945×10^5
105	35,250	3.9	8.945×10^5

TABLE II.

Frequency 882 $\frac{1}{3}$ Kc/Sec.

Temperature in degrees centigrade	Resistance (R.) in ohms	Dielectric constant (K)	Conductivity (σ) in c. s. u.
0	90,500	4.2	3.484×10^5
15	60,500	4.1	1.742×10^6
30	46,000	4.1	6.853×10^5
40	44,250	4.0	7.125×10^5
50	42,500	4.0	7.418×10^5
60	40,500	4.2	7.784×10^5
70	39,500	4.1	7.962×10^5
80	39,000	4.0	8.083×10^5
90	38,500	3.8	8.189×10^5
100	38,000	3.8	8.296×10^5

TABLE III.

Frequency 810.8 Kc/Sec.

Temperature in degrees centigrade	Resistance (R.) in ohms.	Dielectric constant (K)	Conductivity (σ) in c. s. u.
0	91,500	4.2	3.445×10^5
10	75,000	4.2	4.205×10^5
28	50,000	4.1	6.305×10^5
40	44,500	4.0	7.084×10^5
50	42,500	4.0	7.416×10^5
60	41,000	4.1	7.690×10^5
70	40,500	4.2	7.784×10^5
80	39,500	4.1	7.982×10^5
90	37,500	4.0	8.409×10^5
100	38,500	4.0	8.189×10^5
105	38,500	4.0	8.189×10^5

TABLE IV

Frequency 688.5 Kc/Sec

Temperature in degrees centigrade	Resistance (R ₁) in ohms.	Dielectric Constant (K)	Conductivity (σ) in c. s. u.
0	92,500	4.4	3.427×10^5
10	71,000	4.2	4.764×10^5
21	52,500	4.2	6.005×10^5
30	47,500	4.1	6.637×10^5
50	43,000	4.0	7.331×10^5
60	42,000	4.0	7.508×10^5
70	41,500	4.1	7.568×10^5
80	40,725	4.1	7.713×10^5
90	40,500	4.2	7.784×10^5
100	40,500	4.0	7.781×10^5
105	40,000	4.0	7.881×10^5

SUMMARY AND CONCLUSIONS

Dielectric constant and conductivity of soil at radio frequencies have been determined experimentally by measuring the capacitance and resistance of a condenser with soil as dielectric. The change in the dielectric constant and conductivity due to temperature was noted. The constants were measured at different frequencies in the broadcast band. The value of conductivity was of the order of 10^5 c. s. u. and it increased with temperature. For dry soil the conductivity increased from a value of 3.4×10^5 c. s. u. at 0°C to a value of 8.2×10^5 at 105°C .

There is no apparent change in the dielectric constants with rise of temperature and the value is nearly 4.0. The temperature coefficient of conductivity is positive and the value is 2 per cent. per degree centigrade at 20°C . It increases however, with the frequency of the impressed waves. These results show that the conductivity of the soil increases with temperature and also it has been shown previously that it increases with the amount of moisture present.

Thus it may be concluded that the values of conductivity of soil will be higher in summer and rainy season than those in winter.

In conclusion, I wish to record my sincere thanks to Professor P. Dutt, for giving all the facilities for carrying out the investigation and to Dr. S. S. Banerjee for his valuable suggestions during the progress of the work.

REFERENCES

- ¹ Gish, O. H. and Rooney, W. G., *Terr. Magn. and Atmos. Elec.*, **30**, 161 (1925).
- ² Ratcliffe, J. R. and White, F. W. G., *Phil. Mag.*, **10**, 667 (1930).
- ³ Strutt, M. J. O., *Elektr. Nachr. Tech.*, **7**, 387 (1930).
- ⁴ Feldman, C. B., *Proc. Inst. Rad. Eng.*, **15**, 108 (1927) and also **21**, 764 (1933).
- ⁵ Smith-Rose, R. L., *Journ. Inst. Elec. Eng.*, **75**, 221 (1934).
See also Smith-Rose, R. L. and Mc. Petrie, J. S., *Proc. Phys. Soc.*, **46**, 640 (1934).
- ⁶ Khastgir, S. R. and Sengupta, B., *Phil. Mag.*, **22**, 265 (1936).
- ⁷ Banerjee, S. S. and Joshi, R. D., "*Science and Culture*," **2**, 587 (1937).
- ⁸ Banerjee, S. S. and Joshi, R. D., "*Journal of the Benares Hindu University*," **1**, 365 (1937).
- ⁹ Hopkinson, J., *Phil. Mag.*, **2**, 314 (1876).
- ¹⁰ Wagner, K. W., *Ann. der Physik*, **40**, 870 (1913).
- ¹¹ Whithead, J. B., "*Lectures on Dielectric theory and insulation*," published by McGraw Hill Book Company, p. 98 (1927).
- ¹² Higgs, P. J., *Journ. Inst. Elec. Eng.*, **68**, 736 (1930).

COLLEGE OF SCIENCE,
PHYSICS LABORATORY,
BENARES HINDU UNIVERSITY

RAMAN EFFECT IN BORIC ACID AND IN SOME BORON COMPOUNDS

By S. M. MITRA,

Physics Laboratory, Dacca University

(Received for publication, November 15, 1937.)

Plate I

ABSTRACT. The paper gives the results obtained from the author's investigations on Raman effect in boric acid and other borates. In the case of the boric acid solution the frequencies 515, 872 and 986 cm^{-1} and in the case of the solid powder the frequency 882 cm^{-1} in addition of the two broad lines at 3195 and 3200 cm^{-1} due to the vibrations of O-H, were observed. Presumably therefore the molecule B(OH)_3 has a symmetry D_{3h} .

The results obtained in the case of methyl borate, ethyl borate and butyl borate are also included in the report.

INTRODUCTION

In continuation of our investigations on the Raman effect in organic and inorganic compounds ¹ very recently we studied the Raman spectra of boric acid and of a few boron compounds. The present paper gives the report of the same.

EXPERIMENTAL ARRANGEMENT

The substances were studied either in solid and liquid states or in solution and they were all Merck's or Kahlbaum's preparation further purified in the usual way. The method of illumination was virtually the same as that of Wood in the case of the liquids and the solutions. The liquid (or the solution) was put in the inner tube placed inside the outer jacket of the Wood's tube. The whole was clamped upright and a vertical mercury arc lamp was placed alongside, so that the light scattered at right angles emerged along the axis of the vertical tube. The scattered beam was totally reflected by a total reflection prism on to the slit of the spectrograph thereby making the maximum possible illumination. The slit of the spectrograph was guarded from direct illumination by screens and practically the whole light that entered the slit was due to the scattering at right angles.

At the ordinary temperature cold water was continually circulated through the annular space and at the higher temperature hot water from a jar was continually made to pass by a small pump, and two thermometers at the inlet and at the outlet measured the temperature. The continuous band of the exciting light was cut off by adding a little fluorescein to this circulating water.

The plates were all measured with a Hilger travelling microscope and the wave-lengths of the Raman lines calculated by the well-known formula

$$\lambda = \lambda_n \left(\frac{n}{n - n_n} \right), \text{ with the known mercury lines taken as standard.}$$

In the case of some of the plates copper lines were taken as standard.

In the case of the solid powder the usual technique of the complementary colour filters was employed.

RESULTS IN DISCUSSIONS

Boric Acid—Many workers tried to investigate this compound in solution but the intense continuous band due to the fluorescence of the substance stood in their way. Ananthakrishnan² while investigating a few boron compounds found only one frequency at 875 cm.^{-1} in the case of the saturated solution of the acid. In our present investigation we also observed this continuous band, which was so strong that it practically obliterated the faint Raman lines. But as in the case of phosphoric acid observed by Hibben,³ in arsenates and glycerine observed by the present author⁴ and in the amino acids observed by Wright and Lee,⁵ it was found that the addition of KI to the solution removed this band to a considerable extent. The results of our measurements are given in the following table and in plate I. It will be evident from the table that we have observed the following frequencies, viz., $\Delta\nu = 515, 872, 986 \text{ cm.}^{-1}$ in the case of the saturated solution of the acid.

The spectrum of the powdered solid shows a strong line at $\Delta\nu = 882 \text{ cm.}^{-1}$, the other lines found in the case of the solution could not be identified owing to the continuous band. In addition to the aforesaid line there are two broad lines at $\Delta\nu = 3195$ and 3290 cm.^{-1}

TABLE I
Raman frequencies in Boric Acid, $\text{HO-B} \begin{matrix} \text{OH} \\ \text{OH} \end{matrix}$

Substance	Cm.^{-1}		
Boric Acid sol. saturated at 70°C	515 w	872 s	986 w
Boric acid solid	882 s	3195 bs	3290 bs

s—strong, w—weak, b—broad.

Raman Effect in Boric Acid and in some Boron Compounds 11

We might consider the molecule of the boric acid to be analogous to the general type of molecule XY_3 , provided we treat the group OH as a single unit. Such a molecule can have two types of symmetry C_{3v} or D_{3h} according as the structure is pyramidal or coplanar. The symmetric plane structure possesses four vibrations, one totally symmetric vibration which is active in Raman effect but inactive in infra-red, one asymmetric with respect to the plane of the molecule and active in infra-red but inactive in the Raman spectrum, and two doubly degenerate vibrations which are active both in Raman spectrum and in the infra-red. In all, we expect three frequencies in the case of the coplanar structure. These vibrations are 515, 872 and 686 cm^{-1} in the case of the boric acid and hence the acid has the symmetry D_{3h} .

Another interesting fact is revealed in the table, *viz.*, the frequency 872 in the case of the saturated solution which is due to the totally symmetrical vibration of the molecule $\text{B}(\text{OH})_3$ becomes 882 in the case of the solid. Such an increase has also been found by others in the cases of many organic and inorganic substances. As for the vibrations 3195 and 3200 cm^{-1} observed in the case of the powder, they perhaps owe their origin to the vibrations of O-H .

ORGANIC BORATES

In this connection we investigated a few organic borates, the results obtained are tabulated in the following table II. The figures within the brackets indicate the intensities.

TABLE II

Methyl borate.	Ethyl borate	Butyl borate
201 (6)	240 (1)	
	295 (2)	
318 (1)	340 (1)	478 (1)
521 (2)		572 (1)
726 (10)	727 (6)	730 (1)
	750 (1)	
	809 (1)	829 (6)
854 (6)	890 (4)	
	947 (2)	990 (2)
		965 (3)

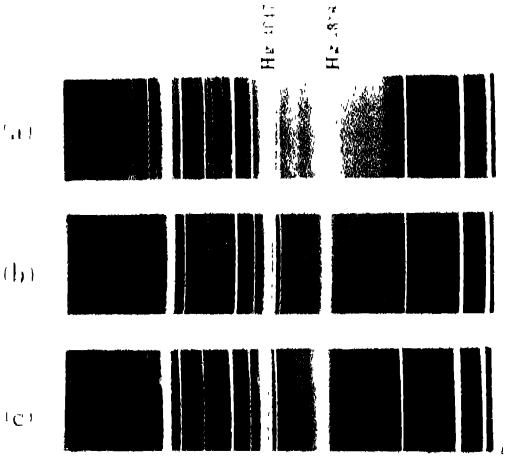
TABLE II (contd.)

Methyl borate.	Ethyl borate.	Butyl borate.
1028 (5)	1050 (4)	1065 (4)
1061 (1)	1090 (5)	
1112 (2)		
	1280 (1)	1358 (4)
	1328 (1)	1315 (1)
	1390 (1)	1310 (6)
	1446 (8)	1450 (8)
1460 (5b)	1486 (2)	
	2864 (8)	2858 (8)
2836 (1)	2898 (8)	2880 (6)
2875 (12)		
2910 (2)	2932 (10)	2940 (8)
2940 (9)		2970 (8)
2975 (4)		
2986 (5b)		
	3046 (6)	

It might be mentioned here that the Raman spectra of a few organic borates were investigated by Joglekar and Thatte⁶ a few years ago and very recently Ananthakrishna⁷ also studied the Raman spectra of methyl and ethyl borates. But there is a great disagreement between them as will be evident from the table III where the values for the methyl and ethyl borates obtained by Joglekar and Thatte and Ananthakrishnan, together with those observed by the present author are given.

TABLE III.

Methyl borate. *			Ethyl borate.		
Author.	J & T.	Anantha.	Author.	J & T.	Anantha.
201		197	240	240	242
318		318	295	273	295
521	488	526	340	323	350
				495	413
				587	531
				615	



Raman Spectra of Boric Acid.

- (a) Solution, saturated at 70°C without potassium iodide.
- (b) Solution, saturated at 30°C with potassium iodide.
- (c) Solution, saturated at 70°C with potassium iodide.

TABLE III (contd.),

Methyl borate,			Ethyl borate,		
Author.	J & T	Anantha	Author	J & T.	Anantha
726	710	718	727	722	727
			750		
			800	855	800
851	800		890	840	802
			917	911	917
1048	1028	1030	1050	1055	1050
1001			1000		1002
1112	1112	1171		1113	
				1160	
				1210	
			1280	1280	1280
			1335	1335	1335
			1390		1390
1400	1450	1460	1440	1457	1440
	1503		1486		1480
	1753			1820	
	1989			1807	
	2028				
2830		2833	2861		2864
2875	2898	2870	2865		2868
2910		2910			
2940	2940	2940	2932	2930	2931
2975		2975		2977	2975
2986		2988			
	3020		3046	3040	
				3118	

We might also consider the molecules of methyl borate $B(OCH_3)_3$ as analogous to the general type XY_3 , provided we treat the group OCH_3 as a single unit. Such a molecule can have, as we have already mentioned, two types of

symmetry C_{3v} and D_{3h} according as the structure is pyramidal or coplanar. In the former case, " C_{3v} ," there should be two totally symmetric and two double degenerate vibrations, all the four being active in the Raman spectrum. These four frequencies are identified to be 210, 318, 521 and 726 cm^{-1} in the case of the methyl borate, which consequently has the symmetry " C_{3v} ." Of the other frequencies, 1028 and 1112 cm^{-1} are probably due to the vibrations of $-\text{OCH}_3$ group and the remaining frequencies are to be ascribed to the hydrogen atoms.

In conclusion the author thanks Prof. S. N. Bose for his kind interest in the work and Dr. B. N. Mitra and Prof. Dr. J. C. Ghose for the chemicals and the spectrograph.

PHYSICS LABORATORY,
DACCA UNIVERSITY.

REFERENCES

- ¹ S. M. Mitra, "*Science and Culture*," **2**, 36 (1936); "*Zeit. f. Phys.*," **98**, 740 (1936) **102**, 607 (1936); **103**, 543 (1937)
- ² R. Ananthakrishnan, "*Proc. Ind. Acad. Sci.*," **4A**, 74 (1936).
- ³ J. Hilben, "*Jour. Amm. Chm. Soc.*," **53**, 2418 (1931).
- ⁴ S. M. Mitra, "*Zeit. f. Phys.*," **93**, 141 (1934).
- ⁵ N. Wright and W. Lee, "*Nature*," **139**, 351 (1937).
- ⁶ M. Joglekar and V. Thatté, "*Zeit. f. Phys.*," **98**, 692 (1936).
- ⁷ R. Ananthakrishnan, "*Proc. Ind. Acad. Sci.*," **4A**, 74 (1936)

ON ANOMALOUS DEPOLARIZATION OF THE LIGHT SCATTERED BY BINARY MIXTURES

By BIRENDRA KRISHNA MOOKERJEE

PART I

(Received for publication, November 30, 1937)

ABSTRACT The distribution of intensity in the "wing" of the Rayleigh line due to a binary mixture of CS_2 and CH_3OH at the critical solution temperature as well as the dependence of the value of ρ_k of the light scattered by a similar mixture of phenol and water on the shape of the illuminated volume have been experimentally investigated. The results do not seem to support the theory of formation of "clusters" put forward by Krishnan.

1. INTRODUCTION

Krishnan¹ has recently observed that the light scattered along the direction of the incident electric vector by some binary mixtures at the critical solution temperature is polarized in a way not expected from the primitive theory of light scattering. Thus it is found that with the incident vibration in the horizontal direction, the ratio of intensity of the horizontal component to that of the vertical may be as much as 5, while from the primitive theory of molecular scattering of light, this should be unity. This anomaly has been explained by Krishnan by assuming that large clusters of molecules are present at and near the critical solution temperature, so that the fundamental assumption in the primitive theory that the size of the scattering particles is small compared to the wave-length of incident light cannot now be made. The theory of scattering by large particles had already been developed by Lord Rayleigh,² Mie,³ and Shulejkin,⁴ and Krishnan based his conclusions on the results of investigation of these authors. Later, Gans,⁵ Vrkljan and Katalinic⁶ have made theoretical investigations on the relation between values of factor of the depolarization and the shape and size of the scattering particles.

The same subject of light scattering along the direction of incident vibration in binary liquid mixtures has however been independently studied experimentally by Rousset,⁷ who also observed the value of ρ greater than 1, and put forward the theory that the anomalous depolarization is due to secondary scattering. There is a fundamental difference between Rousset's explanation and that offered

by Krishnan. Rousset does not assume any definite size of the scattering particles but since he integrates the secondary scattering over the illuminated volume of the liquid, the value of ρ depends on the shape of this illuminated volume. In Krishnan's theory, on the other hand, the secondary scattering is not taken into consideration at all, and since only the primary scattering by large particles is considered the value of ρ should not depend on the shape of the illuminated volume. It is evident therefore that both the explanations cannot be simultaneously correct. It was, therefore, thought worth while to investigate experimentally how the intensity of the wing accompanying the Rayleigh line is affected by the formation of the so called "swarms" in opalescent mixtures and also whether the shape of the illuminated volume of the mixture actually affects the value of ρ , the factor of depolarization of the light scattered in the direction of the incident light vector, and the present investigation was therefore undertaken.

As mentioned before, the experimental study consists of two parts :

(A) In the first part is studied the wing of the Rayleigh line produced by a critical solution of three parts by weight of carbon disulphide and one part of methyl alcohol, with incident unpolarized light.

(B) In the second part is studied the depolarization of the light scattered along the direction of the incident vibration for a critical solution of 34% by weight of phenol in water and for different shapes of the illuminated volume of liquid.

(A) *Wing of the Rayleigh line*

Both the liquids CH_3OH and CS_2 were purified by distillation in double bulbs. The solution of CS_2 in CH_3OH was contained in a vertical glass tube, 2 cms. in diameter and occupied a length of 6 cms. of the tube. A part of this tube was immersed in a glass cell containing water and maintained at the critical solution temperature, *viz.*, about 41°C , by placing a covered electric lamp below. The light from a Hg arc was focussed on to the liquid by a large condenser and the light scattered in a perpendicular direction was spectroscopically analysed. A Fuess spectrograph having optical parts of glass and a dispersion of about $11.5 \text{ \AA}$ per mm. in the region of $4047 \text{ \AA}$ was employed. The spectrum was photographed on a Golden Isozenith plate and the microphotometric record was obtained by means of a Moll self-registering microphotometer. The true intensity curve was then obtained in the usual way from blackening—log intensity curves.

RESULTS

TABLE I.

Intensity Distribution in the Wing for the Critical Mixture
CS₂ + CH₃OH

$\Delta\nu$ in cm. ⁻¹	10.5	21.0	31.5	42.0	52.5	63.0	73.5	84.0
Int.	154.9	106.9	80.7	63.0	51.8	36.7	27.2	19.3

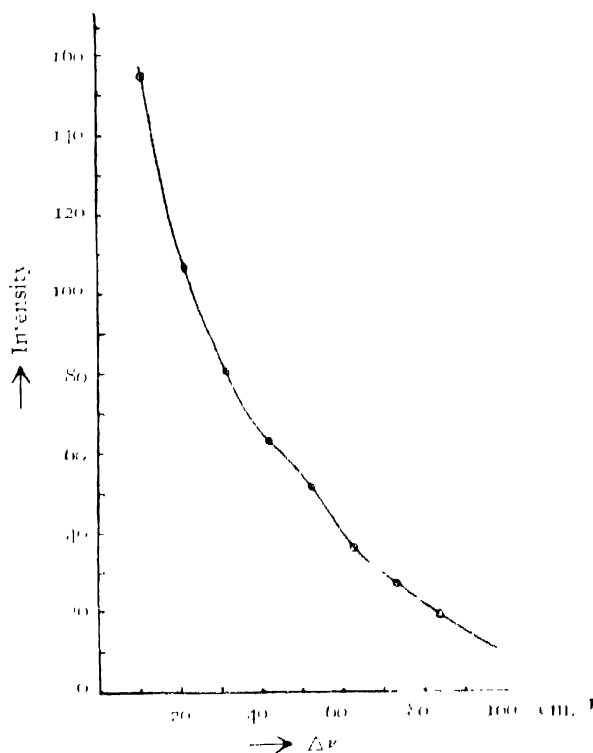


FIGURE 1.

The intensity distribution in the wing on the Stokes side is graphically represented in figure 1. It will be observed that there is an inflection in the curve at about 50 cm.⁻¹ from the centre of the Rayleigh line and the wing extends to about 120 cm.⁻¹ On comparing the plate for the opalescent solution with that due to a 30% solution of CS₂ in CH₃OH no noticeable change in the intensity of the wing relative to the Raman line at 655 cm.⁻¹ was observed.

(B) *Depolarization of Light Scattered in the Direction of Incident Light-Vector*

A 34% solution of Merck's crystallised phenol in distilled water was taken in a rectangular glass vessel which was kept immersed in water in a wide beaker. The beaker was electrically heated by means of some coils of resistance wire placed below and the temperature was maintained at about 65°C which was found to be the solution temperature. The light from a point-o-light lamp was made parallel by a convex lens and then a nicol was interposed in its path so that the incident electric vector was horizontal. The light scattered in a perpendicular direction in horizontal plane was observed through a combination of a Wollaston double image prism and a nicol. For separation of the two components by the Wollaston prism a rectangular slit (1 mm. $\times$ 2 mm.) was interposed in the path of the scattered light, and for better parallelism of the rays another slit of the same size was interposed just before the observation nicol. The ratio of the intensities in the horizontal and vertical components was obtained in the Cornu method by visual observation. If θ be the angle from the horizontal plane to the transmission plane (short diagonal) of the nicol when the two images are of equal intensity then

$$\frac{\text{Intensity of the horizontal component}}{\text{Intensity of the vertical component}} = \tan^2 \theta.$$

The experiment was repeated with different shapes of the illuminated volume of the opalescent mixture.

RESULTS

In one case the illuminated portion of liquid had nearly the shape of a cube of sides 2.8 cms. placed so that two parallel faces were vertical and perpendicular to the incident beam and the other faces made an angle 45° with the vertical. In the other case the illumination volume was of the shape of a rectangular lamina so placed that the four narrow sides were all vertical and all the edges were either parallel or perpendicular to the incident beam. In this case, the sides of the rectangular lamina were 5 cm., 2.8 cm. and 0.4 cm. respectively. The ratio of the length to the thickness of the rectangular lamina was thus about 12. The mean of the several readings for the depolarization factor for the above two cases of the illuminated volume are given in table II.

TABLE II.

Values of ρ for two Different Shapes of Illuminated Volume with Critical Solution of Phenol + Water.

Shape of Illuminated Volume.	θ .	$\rho = \tan^2 \theta$.
Cube	46°	1 (approx.)
Thin Rectangle	60°	3

DISCUSSION

The intensity distribution in the wings for pure CS_2 and for 30% mixture of CS_2 in CH_3OH at the ordinary temperature is given in another paper.⁸ It will be found in all the cases that there is an inflection in the curve at about 50 cm.^{-1} . Further the extension of the wing in the critical solution is also the same as in the pure liquid and in the 30% solution. This shows that the rotation of the molecules which gives rise to the wing is not appreciably diminished in the critical solution. But, if, as postulated by Krishnan, the molecules form clusters of definite shape and size, such as thread-like, then it seems that the rotation of the molecules in these clusters should be much hindered. The absence of such hindrance cannot however conclusively invalidate Krishnan's theory, since even in clusters rotation about some axis may be possible.

On the other hand the observation on the depolarization for different shapes of the illuminated volume cannot at all be explained by Krishnan's theory. According to this theory the depolarization factor should be the same for all shapes of the volume illuminated, as it must, depending only on the shape and size of the molecular clusters. But in the actual experiments described above such divergent values as 1 for a cube and 3 for a rectangular lamina are obtained for the depolarization factor.

This is, however, quite in agreement with Rousset's theory. According to this theory the scattering in the direction of the incident vibration is due at the critical solution temperature, for the most part, to the rescattering of the light scattered from the liquid. At the critical solution temperature the isotropic scattering is very high in proportion to the anisotropic scattering and the depolarization factor for the natural incident light becomes almost zero, as shown by Rousset. Hence the light scattered in the direction of the incident vibration may be supposed as mostly due to the secondary scattering. When the temperature is raised, the secondary scattering diminishes and ultimately the anisotropic scattering predominates. Hence though at temperatures sufficiently removed from that of

critical solution the depolarization in the direction of incident vibration should be perfect, the depolarization at and near the critical solution temperature may not be so.

For a clear understanding of the effect of secondary scattering, we shall go into Rousset's calculation in some detail. Let the incident light vibrate in the direction of the Y-axis which is also the direction of observation. Let the origin of co-ordinate be taken at the centre O of any volume element in the scattering medium and let the polar co-ordinates for the centre M of any other volume element dv be r, θ, ϕ . Consider light scattered from M to O. For this, resolve the light vector V of the primary scattering which vibrates parallel to OY (neglecting anisotropy) into one component, V_1 , perpendicular to the meridian plane through M and another V_2 , tangent to the meridian circle. These two components are respectively proportional to $\cos \phi$ and $\sin \phi \cos \theta$ and their resolved parts parallel to the z- and x-axes are given by

$$\begin{aligned} V_{1z} &= -V \cos \phi \sin \phi & V_{1x} &= 0, \\ V_{2z} &= V \sin \phi \cos \phi \cos^2 \theta, & V_{2x} &= V \sin \phi \sin \theta \cos \theta \end{aligned}$$

The above components are in phase and the square of the electric moment induced parallel to OX and OZ at O, are proportional to

$$\frac{[\sin \phi \cos \phi (\cos^2 \theta - 1)]^2}{r^2} dv \text{ and } \frac{(\sin \phi \sin \theta \cos \theta)^2}{r^2} dv$$

where $dv = r^2 \sin \theta d\theta d\phi dr$.

Thus the intensity of the secondary scattering along OY, resolved parallel to OX and OZ, are given by omitting a common factor in both,

$$X_y = \iiint_V \sin^5 \theta \cos^2 \phi \sin^2 \phi d\theta d\phi dr$$

$$Z_y = \iiint_V \sin^3 \theta \cos^2 \theta \sin^2 \phi d\theta d\phi dr$$

where the integral is to be taken over the illuminated volume V of the scattering medium and the suffix 'y' in the left denotes that the incident light vector is parallel to OY.

If the illuminated volume has the shape of a sphere we shall find from the above formulae that X_y and Z_y have the same values as required by the symmetry. A similar result must also follow when the illuminated volume has any other shape which on being rotated through 90° about the axis of y coincides exactly with its original configuration.

Let the illuminated volume have the shape of a circular disc coaxial with the Z-axis and with centre at O.

Let the radius of the disc be R and its height 2H. The expression for X_u and Z_u become easily integrable on transforming to cylindrical polar co-ordinates and it is found that

$$X_u = \frac{\pi}{4} \left(\frac{3}{4} R \tan^{-1} \frac{H}{R} - \frac{1}{4} \frac{R^2 H}{R^2 + H^2} + H \log_e \frac{H^2 + R^2}{H^2} \right),$$

$$Z_u = \frac{\pi}{4} \left(R \tan^{-1} \frac{H}{R} + \frac{R^2 H}{R^2 + H^2} \right).$$

From these formulæ it will be readily seen that in the secondary scattering the X and Z components are not of equal intensity. If, in particular, H is supposed small compared to R, then the above simplifies into

$$X_u = \frac{\pi H}{8} \left(1 + 4 \log_e \frac{H}{R} \right),$$

$$Z_u = \frac{\pi H}{2},$$

and
$$\rho = \frac{X_u}{Z_u} = \frac{1}{4} + \log_e \frac{R}{H}$$

For $R = 10H$ the above gives $\rho = 2.60$

In the actual experiments, however, of Rousset, as also in the present investigation, the illuminated volume was of the shape of a rectangular parallelepiped. If $2a$, $2b$, $2c$ be the lengths of the edges which are parallel to the co-ordinate axes along OX, OY, OZ respectively, then the values of X_u and Z_u , using cartesian co-ordinates, become

$$X_u = 8 \int_a^a \int_a^b \int_a^c z^2 y^2 (x^2 + y^2 + z^2)^{-\frac{5}{2}} dx dy dz,$$

and
$$Z_u = 8 \int_a^a \int_a^b \int_a^c x^2 y^2 (x^2 + y^2 + z^2)^{-\frac{5}{2}} dx dy dz.$$

Calculating for the case when $\frac{c}{a} = \frac{1}{10}$, Rousset finds that the depolarization factor is 3.0.

The two results of Rousset's theory, *viz.*, (i) that for an illuminated volume symmetrical about the y -axis the depolarization factor should be unity and (ii) that for the rectangular parallelepiped with the dimension, $\frac{c}{a} = \frac{1}{10}$, the depolarization factor should be about $\frac{1}{3}$, are well verified by the present investigation. It is to be pointed out, however, that though the volume in the first case, when $\rho = 1$ was not strictly symmetrical about the y -axis, the deviation from symmetry is not so serious as to materially affect the value of $\rho = 1$.

It thus appears that the anomalous depolarisation of the light scattered by binary mixture at the critical solution temperature may be a geometrical effect arising from secondary scattering rather than the effect of the formation of large clusters of molecules.

REFERENCES

- 1 R. S. Krishnan, *Proc. Ind. Acad. Sci.*, **1**, 211 (1934) ; **2**, 221 (1935).
- 2 Lord Rayleigh, *Scientific Papers*, **5**, 547.
- 3 G. Mie, *Ann. de. Phys.*, **33**, 377 (1908).
- 4 W. Shulejkin, *Phil. Mag.*, **48**, 307 (1924).
- 5 R. Gans, *Phys. Zeit.*, **37**, 91 (1936).
- 6 V. S. Vrkljan & M. Katalinic, *Physik. Zeit.*, **37**, 482 (1936).
- 7 A. Rousset, Thesis, 68 (1935), Paris.
- 8 S. C. Sirkar and B. K. Mookerjee, *Ind. Jour. Phys.*, **10**, 375 (1936).

PART II

Krishnan in a recent paper* has questioned the validity of the explanation put forward by A. Rousset (Theses, Paris, 1935) to account for the anomalous depolarization of the light scattered by binary mixtures at the critical solution temperature. The evidences cited by Krishnan seem not to be conclusive, for reasons stated below.

The first evidence advanced by Krishnan against Rousset's theory is that the depolarization factor ρ with incident unpolarized light for a critical water-isobutyric acid mixture should be, on Rousset's theory, $\rho_u = 0.03\%$, while experi-

*The first part of this paper was written in April, 1937 but could not be published earlier as it formed a part of the thesis for the degree of M.Sc. The second part was written on seeing the paper by R. S. Krishnan (*Proc. Ind. Ac. Sci., A.*, **5**, 577, 1937).

†In this Part we adopt for the depolarization factor the notation used by Krishnan.

mentally this is 1.5%. Such a statement is, however, not correct. Because, firstly, the value .003% is a miscalculation, the value calculated on Rousset's theory with the data assumed by Krishnan is not .003% but .025%. Secondly, the data assumed by Krishnan are again not the correct ones. It will be found on p. 77 of Rousset's *Theses* that the experimental value 1.5% is for the temperature $\Delta T = T - T_{\text{crit}} = 0.15^\circ\text{C}$ and not for the temperature $\Delta T = 1^\circ\text{C}$ as stated by Krishnan and to which the above calculation, .025%, applies. On p. 128 of Rousset's *Theses* are given the data for the Rayleigh constants with white and blue light for the water isobutyric acid mixture for the temperature $\Delta T = 0.4^\circ\text{C}$. We can take the same values for the temperature $\Delta T = 0.15^\circ\text{C}$ without sensible error, and in any case the Rayleigh constant for $\Delta T = 0.15^\circ\text{C}$ should never be smaller than that for $\Delta T = 0.4^\circ\text{C}$.

$$\text{Now} \quad \rho_u = \frac{\text{Horizontal component}}{\text{Vertical component}}$$

Disregarding for the present the orientation scattering we can suppose the primary scattering as completely polarized. Then it follows that the horizontal component is due solely to the secondary scattering while in the vertical component the secondary scattering is negligible compared to the primary scattering. Then we have, remembering that the primary scattering is bluish,

$$\begin{aligned} \rho_u &\sim \frac{R_{\text{white}} \times R_{\text{blue}}}{R_{\text{white}}} \\ &= 0.0\% \text{ (from Rousset's data)} \end{aligned}$$

while the experimental value is 1.5%. The effect of the orientation scattering will be to slightly increase the value 0.0%.

The second evidence cited by Krishnan is that if, after Rousset's theory, the secondary scattering is calculated by the formula

$$\rho_h = \frac{O}{O+S}$$

where ρ_h = depolarization factor with incident horizontal vibration,
 O = orientation scattering,
 S = secondary scattering,

then the secondary scattering is not found to vary at the same rate as the primary scattering (R) which it ought to have according to Krishnan. Both the above formula and the argument are however, incorrect. We should instead have, firstly,

$$\rho_h = \frac{O + \chi S}{O + S}$$

where χ is the depolarization factor of the secondary scattering alone. Secondly, it is not true that S should vary as R , but indeed as R^2 in the absence of any

absorption in the medium while actually there being greater and greater absorption as the critical solution temperature is approached the actual variation follows a more complicated law.

Two other objections raised by Krishnan relate to the dissymmetry of scattering and the λ^4 law. These points have been discussed in detail by Rousset and satisfactorily explained without any recourse to the postulate of "Schwambildung."

The theoretical variation of ρ_u with dimensions of the illuminated volume, on Rousset's theory, is mentioned by Krishnan, but not discussed thereafter. His values as given in table III of the paper, however, shows that ρ_h is the same for two different shapes of the vessel, while according to Rousset's theory such should not have been the case. In our experiment, on the contrary, as mentioned in the first part, we found a definite variation of ρ_h from 33% to 100% as the volume was changed from a rectangular lamina to a cube.

The dispersion of depolarization, as found from table III of Krishnan's paper, is, however, in good agreement with Rousset's theory. For the depolarization factors ρ_u, ρ_v being proportional to R it follows that these values for the blue light should be $\frac{\lambda^4_{\text{blue}}}{\lambda^4_{\text{orange}}}$ times that for orange light.

The variation of ρ_u, ρ_v, ρ_h in the background scattering with distance from the centre of the track of light in the medium is found for a critical phenol-hexane mixture and also for an opalescent caesin solution, and it is thereby concluded by Krishnan, that the two cases are similar. The table given by Krishnan, however, scarcely allow such a conclusion to be drawn. Thus ρ_h for the phenol-hexane mixture increases from 36% to only 40% when the slit is taken from the centre to the periphery of the track while for the case in solution the value increases from 42% to almost the full value 95%. For the same movement of the slit ρ_u for the critical solution increases 9 times while that for the caesin solution increases 13 times and ρ_v for the critical solution increases 9 times while that for the case in solution, 15 times.

Thus the evidences cited by Krishnan do not allow any conclusion to be drawn as to the reality of the molecular clusters, while *the definite proof as to the existence of a considerable secondary scattering clearly shown in the appreciably illuminated background* and the satisfactory explanation of all the optical anomalies by its means constitute a strong argument in favour of the point of view expressed in the first part of this paper.

In conclusion I wish to express my grateful thanks to Prof. D. M. Bose for his kind interest in the work. My best thanks are also due to Dr. S. C. Sirkar for helpful suggestions and guidance.

ON THE THEORY OF LIQUIDS *

By A. GANGULI

(Received for publication, February 4, 1938.)

ABSTRACT A general form of distribution function of molecules is given and special cases for gases, liquids and solids are considered.

The consequences of the different terms in the potential energy as given by London are considered and a qualitative explanation of rotation in liquids and solids, viscosity, polymerisation, formation of glass, secondary structure, etc., is offered.

While some liquids having symmetrical molecules, have the same grouping or clustering of molecules as in solids, others have varying co-ordination number.

Certain simplified expressions for distribution function, cohesion, internal forces, viscosity, etc., are reviewed.

Van der Waal equation is discussed at length and cohesive forces and viscosity are calculated therefrom.

Some relations for viscosity, due to Ginzman, Andrade and others, and time of relaxation are obtained in a simplified manner.

Liquids differ, on the one hand, from gases which have random distribution and on the other, from crystalline solids which have definite geometrical configurations. Some workers¹ suggest a continuity of the three states of matter, pressure and volume being the determining factors. With decrease of volume, inter-molecular forces are brought into play, the molecules form clusters² in the liquid state, the number of clustering molecules progressively increases and finally corresponds to the co-ordination number of particular crystalline form.

X-ray scattering provides a method for determining the distribution of molecules in liquids. Recently statistical methods have also been applied and by suitable choice of the form of interaction potential, distribution curves obtained röntgenoscopically have been theoretically reproduced.³

We start with the distribution function for a canonical ensemble of N molecules (Γ -space)

$$e^{-H/kT} = \frac{1}{N!h^3} \int e^{-H/kT} dq_1, \dots, dp_1,$$

Presented at the Jubilee Session of the Indian Science Congress (1938)

the symbols having their usual significance. The Hamiltonian

$$H = \sum_{i=1}^{3N} \frac{1}{2m} p_i^2 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N-1} V_{ij}$$

the latter being the potential energy (excluding chemical valence force) and is zero for random distribution (ideal monatomic gases).

For a proper understanding of the nature of liquids a more thorough estimate of the potential energy is required. The most general form of the potential is

$$= \frac{A}{r^m} + \frac{B}{r^n}$$

A, B, m and n being constants. According to Lennard-Jones⁴ $m=5, 6$ or 7 and $n=9, 10$ or 11 . Recently London⁵ has shown from quantum mechanical considerations that the exact form of the potential should be as follows:—

$$V_e = \frac{-R/r}{R^6} - \frac{C}{R^6} - \frac{C'}{R^6} - \frac{C''}{R^6} - \frac{d}{R^8} - \frac{e_1 e_2}{R} + H,$$

The above terms are respectively due to repulsion, attraction due to dispersion (involving polarisability and ionisation potential), induction (Debye term), orientation (Keesom effect—operative only when the molecules are permanent dipoles), quadrupole-quadrupole attraction, electrostatic attraction (for ions only) and null point energy. Evaluation of the potential can be carried out for simple molecules, but difficulties are involved in the case of complex molecules.

We shall now consider the effect of these forces. Potential energy is a measure of cohesion and hence, of viscosity, surface tension and heats of fusion and sublimation. With increase of potential energy, rigidity becomes more marked and in the case of complex organic molecules for which short range forces are of the same magnitude as valence forces, instead of melting disruption of molecules takes place, e.g., starch. In some cases the whole system of molecules may behave as a single molecule.⁶ In fact rigidity depends upon the ratio of the inter-molecular to intra molecular binding. For the cases considered above this ratio tends to unity while for inter-molecular weak binding this is small, the molecules being free to move and rotate even in the solid state.⁷ In some highly polymerised amorphous bodies (e.g., rubber), simple units held together by weak van der Waal force may be split up on application of external tension (stretching) and thus give rise to smaller crystalline units.⁸ Repulsive forces are operative at atomic distance and hence may not be so marked in the case of liquids although it is an important factor in the case of close packing of molecules in crystal,

For symmetrical molecules, liquids obtained from monatomic gas, some metals, molecules like CH_4 , C_2H_6 , directive force is absent, clustering corresponds to cubic or hexagonal packing and hence the similarity between crystalline and liquid states as indicated by X-ray scattering. The number of molecules in a cluster in the liquid state may differ under different circumstances thus giving a wide range of co-ordination number.⁹ This variation is largely due to directive force which is exerted between asymmetrical molecules (water, glycerol, long chain compounds, etc.) which may consequently have preferred orientation and anisotropy and may cause the formation of liquid crystals and molecular association. This directive effect is directly proportional to the dipole moment and inversely to temperature and hence with decrease of temperature, the increased attraction will lead to the increase of co-ordination number and conversely with rise of temperature the molecules may rotate and thus cause disorientation. Rotation is favoured if the potential energy and moment of inertia are both small. For instance if n be the oscillational quantum number

$$\begin{array}{llll} n + \frac{1}{2} < \frac{2\pi(\text{IV}_0)^{\frac{1}{2}}}{h} & \dots & \dots & \text{oscillation} \\ & & & \\ & > \frac{2\pi(\text{IV}_0)^{\frac{1}{2}}}{h} & \dots & \dots & \text{rotation.} \end{array}$$

In fact there is a characteristic temperature of transition from oscillation to rotation,

$$T = \frac{2V_0}{K}$$

The variation of co-ordination number in liquids on the average leads to cubic distribution and may explain the intensity of X-ray scattering by liquids. We may thus consider the liquid as consisting of several kinds of configurations. The most stable configuration at absolute zero (no rotation, but vibration persists) corresponding to minimum potential energy, will be closely packed ordered arrangement as in a crystal, the co-ordination number depending upon its geometrical form. With rise of temperature decrease of binding force will cause rotation and hence lead to disorder. At the fusion point liquids may have the same co-ordination number, but molecules may be disordered. Disorder may set in even below fusion point. With further rise of temperature disorder and decrease of co-ordination number both may result. Hence one may consider a liquid as consisting of holes¹⁰ in the crystalline arrangement the deficiency causing disorder and in some cases leading to a secondary structure, the periodicity being repeated after a great interval.¹¹ The unit cell may thus consist of a large number of molecules. A spherical molecules with large dipole moment may retain disordered arrangement to a fairly low temperature, and hence tend to form glass or amorphous bodies.¹²

As a consequence of rotation (due to oriented force) heat of fusion decreases with rise of temperature. Abnormal changes of properties such as specific heat, dielectric constant, viscosity and magnetic susceptibility take place at the transition point. The first two effects have been discussed by Fowler and others.¹³ Viscosity will increase in the case of asymmetrical molecules and thus is akin to the structural viscosity of Ostwald¹⁴ in the case of colloids and liquids. Crystalline diamagnetism decreases due to the orientation of the particles in the magnetic field as has been found in the case of liquid crystals.¹⁵ The so-called size effect on diamagnetic susceptibility may also partly be explained on the basis of orientation of disc or rod shaped particles. As for the other attractive forces inductive effect is least marked, while quadrupole-quadrupole attraction is valid only for limited cases of molecules having permanent dipoles. The coulomb forces are also small at very short distances. The "null punkt" energy is responsible for vibration of molecules even at absolute zero and this may be large enough in some cases. Helium remains an ordered liquid even at the neighbourhood of absolute zero, since the null point energy is greater than the lattice energy.¹⁶

As already mentioned, evaluation of potential is possible only for the simplest cases. Hence several simplified relations have been obtained by several authors by making suitable approximations. We shall briefly discuss some of them.

For simple diatomic molecules, the Hamiltonian may be supposed to be comprised of translational, vibrational and rotational terms. Now introducing quantum conditions we have for a single molecule (μ -space) and taking into consideration available volume, we have

$$e^{-\psi/kT} = \left(\frac{2\pi mk'T}{h^2} \right)^{\frac{3}{2}} f_{\text{rot}} f_{\text{vib}} (v-b)$$

For the case of equilibrium between vapour and liquid molecules

$$\begin{aligned} e^{-\psi_v/kT} &= \left(\frac{2\pi mk'T}{h^2} \right)^{\frac{3}{2}} f_{\text{rot}} f_{\text{vib}} (v-b) \\ e^{-\psi_l/kT} &= \left(\frac{2\pi mk'T}{h^2} \right)^{\frac{3}{2}} (v_v - b) f_{\text{rot}} f_{\text{vib}} e^{-U_0/kT} \end{aligned}$$

Taking rotational and vibrational partition functions to be same in the two cases expressions for vapour pressure may be obtained.¹⁷

Some authors are of opinion that the equation of state of a liquid should involve the melting point. Thus Simon¹⁸ introduces a relationship for internal pressure

$$P = a \left[\left(\frac{T}{T_f} \right)^c - 1 \right]$$

where a and c are constants. $T_c = m.p.$ c has in most cases the value 1. (Bauer, Magat and Sudin¹⁹ introduce a reduced temperature

$$\Theta = \frac{T - T_c}{T_c - T_c} \quad (T_c = \text{critical temperature})$$

and obtain simplified expressions for static properties such as molecular volume, compressibility, surface tension, etc. Huddelston²⁰ postulates a simplified law of force

$$f = a(l - l_0)e^{-b(l - l_0)}$$

where l is the distance between centres of gravity, a , b , l_0 are constants. The above reminds one of Morse's expression for the potential $D e^{-a(r - r_0)} - C e^{-br}$. Huddelston has been able to obtain relation between absolute temperature and thermal expansion, laws similar to Trouton's rule and compressibility at high pressure.

The familiar van der Waal equation has also been used by several workers in studying liquids. Thus internal pressure, cohesion, viscosity and surface tension are all functions of the available volume. That the volume is the determining factor for states of aggregation has been pretty well established. Thus X-ray scattering for gases under pressure resemble that for liquids and solids.²¹ Molecular arrangement in a gas under pressure above critical temperature may be similar to that in a liquid. In fact with decrease in volume as a consequence of increase of pressure, molecular motion becomes restricted until finally the molecules will become rigid when the volume corresponds to that of close packing. The distance of nearest approach $r = kn^{1/3}$, k being a constant and n the number of density. For ideal gas $k = 5.54$ while for a van der Waal gas or liquid, k involves constants a and b and increases until finally it approaches the limiting value unity, corresponding to close cubical packing.

If the internal pressure $\Pi = \frac{a}{v^2}$, we have

$$p + \Pi = \frac{RT}{v - b}$$

Now $\Pi \gg p$. Hence $\frac{a}{v^2} = \Pi = \frac{RT}{v - b}$.

Fair agreement between the values of internal pressure calculated from van der Waal constant and the free space is obtained for several liquids as will be seen from table I.

TABLE I.

Name and formula of liquid.	Mol. Wt.	Specific gravity	Mol. Vol. in c.c.	Available Vol. Mol. Vol.	Available Vol.	$\frac{RT}{V-b}$, $\times 10^{-6}$.	$\frac{a}{V^2} \times 10^{-3}$.	$P = P + \frac{c}{V^2}$ in atm. $\times 10^{-3}$.
Hexane C_6H_{14}	86	0.665	136.4	11.40	16.17	1.333	0.187	0.37
Heptane C_7H_{16}	100	0.684	135.1	10.52	14.53	1.184	0.073	0.63
Octane C_8H_{18}	114	0.7177	158.8	09.1	11.03	1.142	0.168	1.42
Methyl Alcohol CH_4O	32	0.7915	10.42	10.37	1.191	5.143	8.013	8.74
Ethyl Alcohol C_2H_6O	46	0.7891	58.76	09.215	5.37	1.011	3.500	3.49
Propyl Alcohol C_3H_8O	60	0.8035	74.68	06.333	4.403	8.068	2.716	2.03
iso-Butyl Alcohol $C_4H_{10}O$	74	0.8018	91.6	06.61	8.831	2.111	2.0	2.0
Water	18	1	18		0.9100	23.74	18.03	17.5
Mercury	200	13	15.30		2	13.53	44.0	43.3

Numerical values are taken from the tables of Landolt-Bornstein. Values for column 5 are taken from McLeod's paper ²³

In view of the complexity of the forces involved, agreement between Π and $\frac{RT}{V-b}$ is satisfactory. Thus the above equation may be considered to be an approximation to the actual equation of state for liquids.

Now as already mentioned rigidity, surface tension, viscosity are inverse functions of the free space $(V-b)$. These relationships can be deduced in a simple manner. The rigidity

$$\alpha \Pi = \frac{c}{V-b}$$

Again according to Maxwell's theory viscosity $\eta = G\tau$ (τ is the time of relaxation)

$$= \frac{c'}{V-b}$$

The last is Batschinski's relation. ²⁴

A more exact expression for η may be obtained as follows : According to Stokes' law, frictional force

$$f = 4\pi\tau\eta u$$

Now the internal pressure $\Pi = \frac{f}{4\pi r} = \eta \frac{u}{r}$, u being the molecular velocity and r the radius.

Hence $\eta = \Pi \frac{r}{u}$ (Jaeger's Equation) ²⁵

$$= \frac{a}{v^2} \cdot \frac{r}{u} = \frac{RT}{v-b} \cdot \frac{r}{u}$$

For small u (great rigidity) and larger r , η becomes large.

In the case of liquids thermal motion is neither purely translatory as in ideal gases nor purely oscillatory as in crystalline solids but rather a sort of jerky translatory motion. ²⁶ We may introduce an analogy with unimolecular reaction velocity, the activation energy E_a to be overcome here is equal to the cohesive force between the molecules. We thus have Arrhenius equation for the velocity coefficient

$$k = Ae^{-E_a/kT} \text{ and } u = kN = NAe^{-E_a/kT} = ce^{-E_a/kT}$$

$$\text{Hence } \eta = \frac{a}{cr} e^{E_a/kT} = Be^{E_a/kT}$$

This is the relation first obtained by Guzman. ²⁷

More rigid expressions for velocity coefficient has been obtained by the author and others, ²⁸ considering two different systems having different degrees of motion. If we consider the vibrational degree of freedom suppressed during motion and an extra degree of freedom due to translation introduced, we have

$$k = d \left\{ \frac{2\pi mk'T}{h} \right\}^{\frac{1}{2}} \left\{ \frac{k'T}{2\pi m} \right\} e^{-\frac{E_a + \frac{1}{2}h\nu}{kT}} \left\{ 1 - e^{-\frac{h\nu}{kT}} \right\}$$

$$\tau = Nd \frac{k'T}{h} e^{-\frac{E_a}{kT}} \left\{ 1 - e^{-\frac{h\nu}{kT}} \right\}; \quad E_a = E_a + \frac{1}{2}h\nu$$

taking into consideration the null point energy.

$$\text{Hence } \eta = \frac{a}{v^2} \cdot \frac{\tau}{d} \cdot \frac{h}{Nk'T} e^{\frac{E_a}{kT}} \left\{ 1 - e^{-\frac{h\nu}{kT}} \right\} \quad \text{and}$$

The above reduce to the previous equation for large T .

We may obtain expressions for time of relaxation from the values of η . For Newtonian liquids

$$\eta = S / \frac{du}{dt}$$

S being the shearing stress. This is identified with Maxwell's Equation if $S = G$

$$\frac{du}{dt} = \frac{u}{\tau} = -\frac{1}{\tau}, \text{ i.e. } \tau = \tau_0 e^{-t/\tau}; \left\{ dt/dt = u \right\}$$

which is true from the very definition of relaxation time.

Thus putting $G = H$ we have $\tau = \frac{\eta}{H} = \tau_0 e^{\frac{E_a}{kT}}$

a relation obtain by Frenkel.²⁰ We may similarly derive expression for diffusion constant which again decreases exponentially with temperature.

CHEMICAL LABORATORY,
COLLEGE DUPLIN, CHANDERNAGORE

REFERENCES

- ¹ Frenkel, J., *Acta Physicochim. U. R. S. S.*, **3**, 633, 613 (1935); *Nature*, **136**, 167 (1935).
Herzfeld, K. F. and Mayer, M. G., *J. Chem. Phys.*, **2**, 38 (1934).
- ² Mayer, J. E. and Ackermann, P. G., *ibid.*, **5**, 67, 74 (1937).
- ³ Kirkwood, J. G. *ibid.*, **3**, 300 (1935); *Chem. Rev.*, **19**, 275 (1937).
Mayer and Ackermann, *loc. cit.*
- ⁴ Lennard-Jones, J. E., *Proc. Roy. Soc. (London)*, **A**, **106**, 441 (1924).
- ⁵ London, F., *Trans. Farad. Soc.*, **33**, 8 (1937).
- ⁶ Slater, J. C. and Frank, N. D., *Theoretical Physics (Mc. Graw-Hill)*, 1st ed., p. 448.
- ⁷ Pauling, L., *Phys. Rev.*, **36**, 435 (1936); Stern, T. S., *Proc. Roy. Soc. (London)*, **A**, **130**, 551 (1931).
- ⁸ Katz, J. R., *Trans. Farad. Soc.*, **32**, 83 (1936).
- ⁹ Prius, J. A. and Petersen, H., *Physica*, **3**, 147 (1936); Rawlins, F. I. G., *Trans. Farad. Soc.*, **29**, 977 (1933); Bernal, J. D., *ibid.*, **33**, 27 (1937).
- ¹⁰ Hyring, H., *J. Chem. Phys.*, **4**, 282 (1936).
- ¹¹ Bragg, W. H., *The Solid State (Internal conference)*, p. 114.
Zwicky, F., *Rev. Mod. Phys.*, **4**, 193 Ganguli, A., *Current Sc.*, **4**, 128 (1936) *Z. f. Krist.*, **96**, 225 (1937).
- ¹² Zachariasen, W. H., *J. Amer. Chem. Soc.*, **54**, 3841 (1932); Ganguli, A., *Z. f. Krist.*, **97**, 88 (1937).

- 13 Fowler, R. H., *Proc. Roy. Soc. (London)*, **149**, 1 (1935).
Frenkel, J., *Acta, Physicochim. U. R. S. S.*, **1**, 97 (1935).
- 14 Ostwald, W., and co-workers, *Koll. Zeits.*, **60**, 159 (1932) and other papers in the same journal.
- 15 Foex, G., *Trans. Farad. Soc.*, **29**, 958 (1931).
- 16 Simon, P., *Nature*, **133**, 520 (1934).
- 17 Newton, R. P., and Eyring, H., *Trans. Farad. Soc.*, **33**, 73 (1937).
- 18 Simon, P., *ibid.*, p. 65.
- 19 Bauer, E., Magat and Sudin, *ibid.*, p. 81.
- 20 Huddleston, I. J., *ibid.*, p. 97.
- 21 Compton, A. H. and Allison, S. K., *X-rays in Theory and Experiment* (Macmillan), 1st ed., p. 174.
Harvey, G. C., *Phys. Rev.*, **46**, 411 (1934).
- 22 Raman, C. V., *Phil. Mag.*, **47**, 671 (1924); Gans, R., *Phys. Z.*, **23**, 168 (1922).
- 23 McLeod, D. B., *Trans. Farad. Soc.*, **19**, 6 (1923).
- 24 Batschinski, Z., *J. Phys. Chem.*, **84**, 613 (1918); McLeod, D. B., *Trans. Farad. Soc.*, **19**, 6 (1923).
- 25 Herzog, R. O. and Kudar, H., *Z. f. Phys.*, **80**, 217 (1933).
- 26 Frenkel, J., *ibid.*, **35**, 664 (1926).
- 27 Andrade, A. N. C., *Phil. Mag.*, **17**, 497, 668 (1931).
Kudar, H., *Phys. Z.*, **35**, 360 (1934).
Sheppard, *Nature*, **125**, 489 (1930); Frenkel, J., *ibid.*, 581.
- 28 Ganguli, A., *Phil. Mag.*, **12**, 583 (1931).
Eyring, H., *J. Chem. Phys.*, **3**, 107 (1935); Polanyi & Evans, *Trans. Farad. Soc.*, **31**, 875 (1935), **32**, 1333 (1936).
- 29 Frenkel, J., *ibid.*, **33**, 58 (1937).

new lines are due to lattice oscillations and these oscillations in quasi-crystalline groups of molecules present in the liquid state are also responsible for the appearance of the wing accompanying the Rayleigh line due to liquids. Vuks² next reported the results of the study of the Raman spectra of *p*-dichlorobenzene at different temperatures and assuming that there are two modifications of this crystal and that transformation from one modification to the other takes place with the change of temperature, he concluded that the positions of the new lines depend on the nature of the lattice. It was shown later on by the present authors,³ however, that the Laue pattern of a single crystal of *p*-dichlorobenzene remains unchanged with the change of temperature of the crystal, showing thereby that the lattice remains the same though the positions of the new Raman lines shift with such a change of temperature. Vuks⁴ next studied the Raman spectra of mixed crystals containing different proportions of *p*-dichlorobenzene and *p*-dibromobenzene and concluded that the new lines are due to lattice oscillations because they behave exactly in the same way as the "reststrahlen" frequencies and of mixed crystals of KCl and NaCl. Sirkar and Bishui⁵ have recently repeated these investigations and have failed to confirm the above conclusions drawn by Vuks. It has again been shown by Sirkar⁶ that according to selection rules, Raman lines due to lattice oscillations are forbidden in the case of crystals of naphthalene, *p*-dichlorobenzene and *p*-dibromobenzene. It has also been pointed out by him that since the new lines observed with these crystals are sometimes more intense than the most intense Raman lines due to intra-molecular vibrations in the respective molecules, these new lines cannot be due to lattice oscillations.

Further investigations have been made recently by the present authors and the results obtained in these investigations have bearing on the hypothesis regarding the origin of the new lines observed in the Raman spectra of molecules in the solid state in the low-frequency region, and also on the hypothesis regarding the origin of the "wing" due to liquids. It is the purpose of the present paper to discuss in detail how far these results as well as those of previous investigations lead to a definite conclusion regarding the origin of the new lines as well as of the "wing." Part I of the present paper deals with the question whether the new lines due to crystals are in any way associated with the lattice oscillations and Part II deals with the question whether the "wing" due to the liquids are in any way related to the new lines mentioned above.

PART I

THE ORIGIN OF THE NEW RAMAN LINES OBSERVED WITH MOLECULAR CRYSTALS

The hypothesis put forwarded by Gross and Vuks that the new Raman lines observed with organic crystals are due to lattice oscillations can be tested in

various ways. First, when the crystal structure is known it can be easily ascertained whether Raman lines due to lattice oscillations are forbidden according to selection rules or not. Secondly, when any change is observed to take place in the properties of the new Raman lines with the change of temperature of the crystals, it can be ascertained by investigations other than the study of the Raman spectra, whether the crystal structure changes with such a change of temperature or not. Thirdly, when the same substance is known to exist in two different crystalline forms it can be ascertained whether the positions of the new lines are identical in the two cases or not.

(a) *Selection rules for lattice oscillations in Raman effect cannot account for the observed intensities of the new Raman lines*

As mentioned above, evidence has been put forward by Sirkar⁷ to show that the new Raman lines are very intense in some cases in which the Raman lines due to lattice oscillations are forbidden according to the selection rules. The results obtained with solid carbon dioxide recently by the present authors⁸ furnish additional evidence to this effect. It has been observed that in the Raman spectrum of solid carbon dioxide there is a new line at 58 cm^{-1} having an intensity almost twice as much as that of the line 1388 cm^{-1} . The crystal structure of solid carbon dioxide is known.⁹ There are four molecules in the unit cell of the face-centred cubic lattice. The positions of carbon atoms are at $0\ 0\ 0$, $\frac{1}{2}\ \frac{1}{2}\ 0$, $\frac{1}{2}\ 0\ \frac{1}{2}$ and $0\ \frac{1}{2}\ \frac{1}{2}$, and these points are also the centres of symmetry. If the lattice through one of these points oscillates against the rest, there cannot be any asymmetric restoring force and therefore such an oscillation can not produce any Raman line of such a large intensity as has actually been observed. Hence the observed new Raman line can not be due to lattice oscillation.*

* After the communication of this paper for publication, Venkateswaran (*Current Science*, **6**, 378, 1938) has put forward some suggestions regarding the origin of this new Raman line of CO_2 . He has pointed out that this new line may be due to flexural oscillation of the lattice which involves translational as well as angular oscillations of the molecules about equilibrium orientation. It was pointed out long ago by Roussset (*Jour. de Phys.*, **6**, 515, 1935) that the intensity of Raman line due to the angular oscillation or to the hindered rotation postulated by Bhagavantam (*Proc. Ind. Acad. Sc. A.*, **2**, 63, 1935) is negligible. Venkateswaran has not stated whether the flexural vibration postulated by him can produce such large intensity of the new Raman line as is actually observed, but he has stated that the intensity has to be worked out theoretically. Before going into the theoretical calculations it can be seen from simple considerations, however, that the intensity due to angular oscillation alone is less than that due to the δ -oscillation (ν_2) of the CO_2 molecule, and as this latter frequency is usually forbidden in Raman effect, the line due to pure angular oscillation is also forbidden. The translational component of the motion does not produce in this case any change in polarisability, and so the Raman line due to the flexural vibration of the lattice is forbidden. Hence the intense new Raman line is not due to the flexural vibration of the lattice.

The Raman spectra of a few more organic substances, *viz.*, toluene, xylene (mixture of *o*-, *m*- and *p*), *cis* and *trans* dichloro-ethylene and ethylene dichloride have been studied in the solid state at the temperature of liquid oxygen. In the case of solid toluene there is no intense new Raman line in the low frequency region though there may be a very faint line with $\Delta\nu$ less than 40 cm^{-1} . The presence of this line could not be definitely ascertained but there is no uncertainty about the absence of any new line in the region beyond 40 cm^{-1} from the Rayleigh line up to about 150 cm^{-1} . The crystal structure of solid toluene is not known but it can be easily seen that whatever be the arrangement of molecules inside the crystal there cannot be any symmetrical restoring force when the lattice through one set of molecules vibrates against that through another set, because the molecule itself has no centre of symmetry. This is illustrated in figure 1 in which

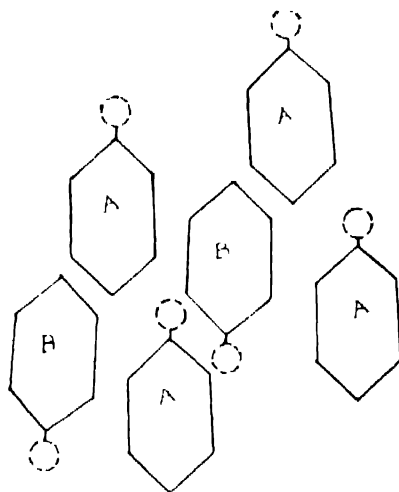


FIGURE 1.

the unit cell is assumed to contain two molecules marked A and B respectively. The restoring force on the side of the CH_3 group is expected to be different from that on the diametrically opposite side and therefore some change in polarisability is expected to occur during the oscillation of the lattice through the molecules marked A against that through the molecules marked B. Since no new Raman line of appreciable intensity is observed in this case, it may be concluded that probably in the case of such molecular lattices no appreciable change in polarisability takes place during lattice oscillations even when the restoring force is asymmetric. Probably the force is too small to produce the change in polarisability. Therefore in the case of centro-symmetrical molecules, *e.g.*, *p*-dichloro- and *p*-dibromobenzene, there is still less chance for the appearance of Raman lines due to lattice oscillations. The above facts seem to lend additional support to the view that the intense new Raman lines observed in the low frequencies region in

the case of centro-symmetrical molecules in the solid state are not due to lattice oscillations.

The results of the investigation of the Raman spectra of crystals of sodium tartarate and tartaric acid made recently by Gupta¹⁰ further corroborate the views set forth above. He has observed that even when the ordinary Raman lines due to intra-molecular oscillations are recorded with larger density in the spectrogram due to sodium tartarate than in that due to tartaric acid, there is no new Raman line in the vicinity of the Rayleigh line in the former case and there are a few intense new Raman lines in this region in the latter case. In the former case, as the lattice is ionic, the restoring force is stronger than that in the latter case in which the lattice is molecular. There is, therefore, less chance for the appearance of the Raman lines due to lattice oscillations in the latter case. The intense new lines observed in the latter case, therefore, cannot be due to lattice oscillations.

(b) The positions of the new lines change even when the crystal structure remains the same

The first attempt to prove that the positions of the new lines shift with change in the crystal structure was made by Vuks.² As already mentioned, his conclusions were not supported by the results of X-ray analysis of the crystals of *p*-dichlorobenzene at different temperatures made by the present authors. It was found by the present authors that the lattice of these crystals remains the same at the two temperatures at which the positions of some of the new Raman lines are observed to be different. It could not be decided from the study of the Laue patterns, however, whether any change in the orientation of the molecules takes place with the change of temperature. This question has been investigated recently by the present authors and the results are discussed below.

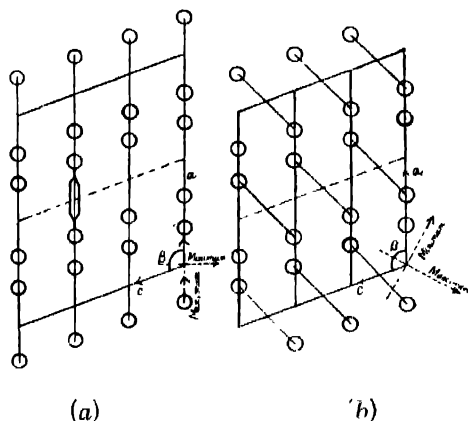


FIGURE 2.

The crystal structures of *p*-dichlorobenzene and *p*-dibromobenzene have been analysed by Hendricks¹¹. Both the crystals belong to the monoclinic prismatic class and the dimensions of the unit cell are almost the same in the two cases. The orientations of the molecules in the unit cell are, however, different in the two cases as shown in figures 2(a) and 2(b) which show respectively the projections of the unit cells of *p*-dichlorobenzene and *p*-dibromobenzene in the *ac*(010) plane. In the case of these compounds containing the benzene nucleus, the directions of vibrations of the light vector for the maximum and minimum refractive indices are respectively in and perpendicular to the plane of the molecule. In the case of *p*-dichlorobenzene these directions are respectively parallel and perpendicular to the *a* axis as shown in figure 2(a). If the molecules would rotate from their positions shown in figure 2(a) to occupy the positions shown in figure 2(b), there would not be any change in the lattice, but the directions of vibrations of the light vector for maximum and minimum refractive indices would change and become as shown in figure 2(b). It is well known that in the case of monoclinic crystals, the *b* axis coincides with the β -axis of the optical ellipsoid. If the rays pass along the β axis, through the crystal, the directions of vibrations are along the major and minor axis of the ellipse AC A'C' as shown in figure 3. These are also the directions for maximum and minimum refractive indices respectively. Hence if the rays travel along the *b* axis of this crystal, the directions of vibrations of the two components in the crystal are along the directions for maximum and minimum refractive indices respectively. If the crystal be examined under a polarising microscope, these directions will be also the directions of extinctions if the incident light pass along the *b* axis of the crystal. Any change in the orientation of the molecule will cause a change in these directions of extinctions, and therefore, by studying the directions of extinctions at different temperatures, it can be decided whether any change in the orientation of the molecules take place with the change of the temperature of the crystal.

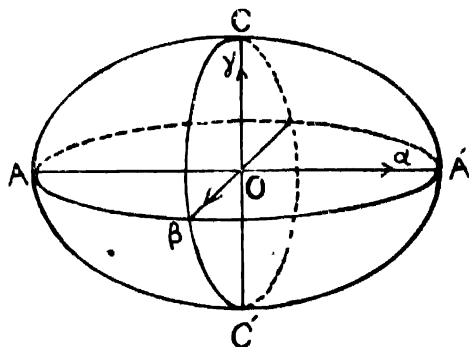


FIGURE 3.

Single crystals of *p*-dichlorobenzene were obtained by crystallisation from alcoholic solution. These were fairly thick plates bounded by (100) faces elongated

along c axis, 110 and 001 faces being also developed. The 010 faces were not developed in these crystals, but a pair of such faces could be obtained by grinding the crystal with linen soaked in benzene. The crystal was then examined under a Leitz polarising microscope with the incident beam parallel to the ' b ' axis. At the room temperature (30°C) the directions of extinctions were observed to be parallel and perpendicular to the a axis. The thin glass plate on which the crystal was resting was next placed on a large piece of melting ice. After about fifteen minutes the glass plate containing the crystal was placed exactly in the same position on the stage as before and the crystal was again examined quickly under the polarising microscope when it was still at the lower temperature, and the directions of extinction were observed to be the same as before cooling. The molecules, therefore, do not rotate with the change of temperature and the orientation is the same at all temperatures as found by Hendricks from X-ray analysis. As it has been observed that the positions of some of the new lines as well as of the lines 305 cm^{-1} and 330 cm^{-1} due to intra-molecular vibrations shift slightly with the above change of temperature, it is evident that such a shift is not connected in any way with the crystal structure.

(c) *The new lines do not shift with change of crystal structure*

The results obtained in the present investigation in the case of solid *cis* and *trans* dichloroethylene furnish evidence to show that the new lines do not undergo any changes even when the lattice changes. It has been observed that in the case of both these substances in the solid state at the temperature of liquid oxygen, there is a fairly intense line at 53 cm^{-1} . Though the crystal structures of these substances are not known it is highly probable that the symmetry elements of the two molecules being different, the crystal structures are also different. Since the new Raman line appears in the same position in both the cases it is evident that the position of this line does not depend on the crystal structure and therefore the line cannot be due to lattice oscillation. In the case of *trans*-dichloroethylene, again, as the molecule is centro-symmetrical, there is some chance for the restoring force during lattice oscillation to be symmetric and therefore the Raman line due to lattice oscillation is probably forbidden in the case.

(d) *An alternative hypothesis regarding the origin of the new lines*

An alternative hypothesis regarding the origin of the new lines was first put forward by Sirkar.^{1,2} It was suggested that these new lines might probably be due to intermolecular vibrations in groups of molecules, there being weak electronic binding among different molecules in each group. Though no other

direct evidence for the presence of such polymerised groups has been put forward except some changes in the positions of ultra-violet absorption bands observed in some cases with the change of state, the properties of the new Raman lines can be explained satisfactorily by such a hypothesis. If the strength of the weak intermolecular bond be appreciably affected during intermolecular oscillations the change in polarisability is also expected to be large and thus the large intensities of the new lines can be accounted for. Again if these states of binding be quantised there may be two such probable neighbouring quantised states in the case of *p*-dichlorobenzene and probably the transition from one to the other takes place with the change of temperature or with the addition of a small quantity of impurity so that the strength of the binding is slightly altered and consequently the frequencies of the Raman lines due to intermolecular oscillations are slightly altered. Also the shift of the line 305 cm^{-1} and 330 cm^{-1} with the change of temperature clearly shows that some change takes place in the C-Cl binding, because these lines are due to C-Cl oscillation. Again, according to the above hypothesis, the nature of the weak electronic binding among molecules should depend only on the nature of the molecule and if the same molecule exists in two forms, the strength of the binding is expected to be the same in the two cases. Thus the fact that the frequency of the new Raman line observed in the case of *cis* dichloroethylene is the same as in the case of *trans* dichloroethylene is explained by the above hypothesis. Thus it may be concluded that though it is difficult to explain the observed facts by the hypothesis that lattice oscillations give rise to the new Raman lines, the new alternative hypothesis of the existence of weak electronic binding among different molecules in groups present in the solid state can explain all the observed facts fairly satisfactorily. It may be mentioned here that the binding being very weak, it may not be possible to detect its presence by x-ray analysis.

PART II

THE ORIGIN OF THE "WING" ACCOMPANYING THE RAYLEIGH LINE DUE TO LIQUIDS

It was first suggested by Gross and Vuks¹³ that the portions of the wing beyond 20 cm^{-1} from the Rayleigh line observed in the case of naphthalene, diphenyl ether, benzene and *p*-dibromobenzene are due to lattice oscillations in quasi-crystalline groups present in the liquid state. They also drew the general conclusion that the major portion of the wing observed in the case of liquids owes its origin to those lattice oscillations in quasi-crystalline groups. Such a hypothesis can, however, be tested in various ways. First, if any portion of the wing due to a liquid be due to the lattice oscillations, this portion ought to be

absent or very faint in the spectrum of light scattered by a dilute solution of the same liquid in a solvent which itself does not produce any wing of appreciable intensity. This question was experimentally investigated by Sirkar¹⁴ and also by Sirkar and Mookerjee.¹⁵ Those authors studied the Raman spectra of solutions of benzene, in methyl alcohol and cyclohexane and of carbon disulphide, chloroform, xylene, acetone and chlorobenzene in methyl alcohol, the dilutions being such that the ratio of the number of molecules of the solvent to that of the solute varied from 5 : 1 to 10 : 1. In none of these cases any diminution in the relative intensity of any portion of the wing with respect to that of any Raman line was observed to take place on dissolving the liquid in the solvent and on the contrary, the intensity of the wing was observed to increase in some cases. These facts do not support the hypothesis that any portion of the wing is due to lattice oscillations.

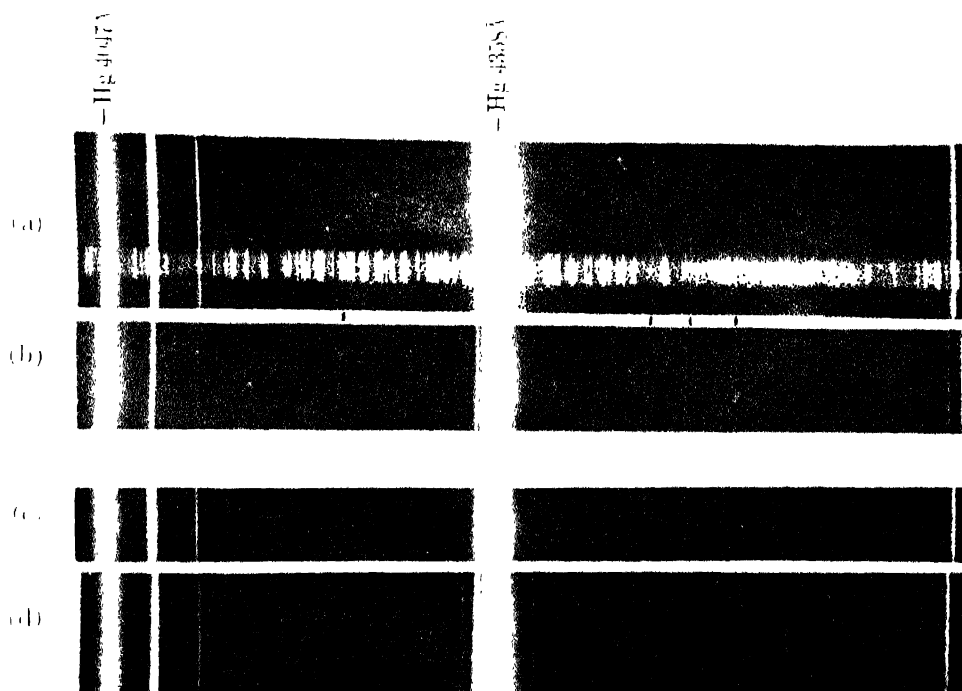
Secondly, if the wing and the new Raman lines have the same origin, there must be correspondence between the intensity of the wing and that of the lines and to some extent between the positions of maximum extensity in the wing and those of the lines. It has been pointed out by Sidorova¹⁶ that (1) in many cases there is correspondence between the intensity of the wing and that of the new lines and that (2) the lines spread out and their positions shift as the crystalline binding is loosened in the liquid state. These conclusions have, however, been drawn from the results of the study of only a few substances and these studies are also of qualitative nature. It will be seen from what follows that results of detailed quantitative investigation do not support the conclusions arrived at by Sidorova from studies of qualitative nature. The integrated intensity of the portion of the wing beyond 10 cm.^{-1} from the centre of the Rayleigh line relative to that of a particular Raman line in each case has been investigated by Mookerjee¹⁷ for a few liquids, *viz.*, acetone, xylene, carbon-disulphide, chlorobenzene and chloroform. The width of the slit of the spectrograph used by him was about 0.15 mm. so that actually the slit was too narrow to give the maximum intensity even in the case of a sharp Raman line in the spectrogram. Since with further increase in the width of the slit the intensity of the Raman line would increase less rapidly than that of the wing, it is evident that with a wider slit the ratio of the intensity of the wing to that of a sharp Raman line would be greater than that obtained with the narrow slit. Even with the narrow slit he got the values given in table I. The ratio of the visually estimated integrated intensities of all the new lines observed in each case to that of the particular Raman line which was used as comparison in the case of the liquid is also included in the table. These values are obtained from spectrograms obtained by the present authors in previous investigations as well as in the present investigation.

TABLE I.

Substance	$\frac{I_{\text{wing}}}{I_{\text{R.L.}}}$	$\frac{I_{\text{new lines}}}{I_{\text{R.L.}}}$
Acetone	6	...
Xylene	42	6
Carbon disulphide	12	3
Chlorobenzene	25	4
Chloroform	8	2

It will be seen from table I that even in those cases in which the wing as well as the new Raman lines are intense, the intensity of the latter forms only a small part of the integrated intensity of the portion of the wing beyond 10 cm^{-1} . Some evidence has again been furnished by some results of the present investigation to show that the new lines are almost absent in the case of the solid state though the wing is very intense in the liquid state. The wing due to toluene is very intense as can be seen from plate II, but there is no new Raman line of any appreciable intensity in Raman spectrum of solid toluene. It has also been observed that the wing due to liquid ethylene dichloride is more intense than that due to *trans*-dichloroethylene but the new line observed at about 60 cm^{-1} in the case of solid ethylene dichloride at the temperature of liquid oxygen is very faint though the new line observed in the case of solid *trans*-dichloroethylene is more intense than the most intense Raman line due to intra-molecular vibration in this molecule. These facts show that there is actually no correspondence between the wing and the new line as far as the integrated intensity is concerned.

As regards the relation between the positions of the new lines in the case of the solid state and those of the region of maximum intensities in the wing due to the liquid state, it was first pointed out by Sirkar¹⁸ that in many cases the intense portion of the wing is nearer to the Rayleigh line than the new lines observed in the solid state. Sidorova,¹⁹ however, has explained this discrepancy by assuming that as the lattice binding becomes a little loose in the liquid state, the corresponding Raman lines not only spread out but also shift towards the Rayleigh line. Consideration of the intensity of such lines shows that probably such a hypothesis is not correct. It is well known that the change in polarisability of individual molecules taking place during lattice oscillations determines the intensity of the corresponding Raman line. Such a change in polarisability takes place only when the restoring force is asymmetric and therefore depends also on



RAMAN SPECTRA.

- (a) Solid toluene at -180°C .
- (b) Liquid toluene at room temperature.
- (c) Dichloroethane at room temperature.
- (d) Dichloroethylene (*trans*) at room temperature.

the magnitude of this restoring force. According to Sidorova this force becomes smaller in the liquid state. In that case the intensity of the corresponding Raman line should also become smaller and smaller as the line would move nearer and nearer to the Rayleigh line owing to the weakening of the crystalline forces. Taking a particular example, *e.g.*, that of carbon disulphide, it can be seen from figure 4 in which the distribution of intensity in the wing has been represented by the curve *a*, that the region of maximum intensity lies within 15 cm^{-1} from the Rayleigh line and that the farthest edge of the wing is at about 120 cm^{-1} . In the case of solid carbon disulphide at the temperature of liquid oxygen there are an intense new line at 70 cm^{-1} and another faint line at about 80 cm^{-1} . If this intense line would spread out to form a continuous wing in the case of the liquid state, the intensity of the wing would gradually diminish towards the Rayleigh line and the distribution of intensity would be somewhat like that shown by the curve *b* in figure 4. Such a distribution cannot account for the actual intensity observed and shown by the curve *a*.

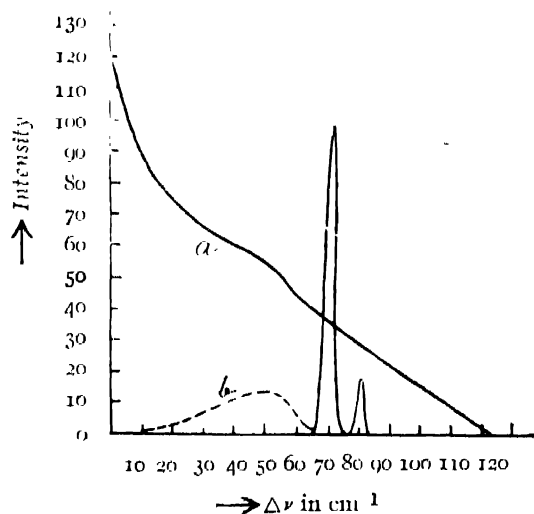


FIGURE 4.

Again, if according to Sidorova the new line observed in the case of the solid state spreads out in the case of the liquid state, it can shift only towards the Rayleigh line and in no case can it move further away from the Rayleigh line. A considerable portion of the wing, however, extends beyond 80 cm^{-1} in the case of carbon disulphide and this portion of the wing cannot be accounted for at all by the hypothesis put forward by Sidorova.

Finally, in many cases the wing is observed to be very intense though the Raman lines due to lattice oscillations are forbidden according to selection rules. If there be so much freedom of movement of the molecules that the symmetry of

account of the fact that these regions hitherto accessible only to spectroscopic observations are now amenable to experimental investigation by the radio waves. Such studies, for instance, yield information regarding the number of collisions between electrons and neutral gas molecules taking place at certain measurable levels—the E and F levels of the upper ionosphere. Since, according to the classical theory, the frequency of such collisions depends upon the pressure and the temperature it seems possible to make an estimate of one or other of these quantities by making suitable assumptions.

These estimates, however crude or rough they may be, when coupled with the knowledge regarding the constituents derived from study of the light of the polar and non-polar aurora and also the possible temperature of the upper regions obtained from both spectroscopic and radio observations are extremely helpful in indicating the lines on which theoretical calculations should proceed for obtaining the most probable density and temperature distribution in the uppermost layers of the atmosphere.

Since the observational data from which such calculations were hitherto made were only those obtained near the lowermost levels of the atmosphere, the results of pioneer theoretical investigators like Wegener,¹ Chapman and Milne,² Maris³ and others, for want of any guiding information as to the actual conditions existing in the upper atmosphere, vary widely from one another. How greatly the calculated results differ from those obtained from later observation is shown by the fact that in the pioneer work of Wegener in 1911 we find that the upper atmosphere is shown as consisting wholly of hydrogen and helium. We now know from spectroscopic evidence that these gases are totally absent in the upper atmosphere. Again to take a particular case at random the atmospheric density at a level of 200 km. as given by various investigators varies even by several orders. It is now possible to greatly reduce the limits of these uncertainties if the results obtained from experimental investigations and observations are taken into account before proceeding with the theoretical calculation.

In the present paper an attempt will be made to calculate the density distribution of the gases in the upper atmosphere—above 100 km.—by utilising the newer knowledge which we have recently gained from the radio experiments and from spectroscopic observations. Calculation of the total quantities of the different constituents which are present above certain definite levels will also be given since a knowledge of this is very important for proper understanding of the absorption of the different spectral regions of the solar radiation which are responsible for producing the various ionised layers of the upper atmosphere.

There are two ideal cases for which calculations regarding the density and the composition of the upper atmosphere can be made very simply starting from the knowledge of these quantities at the ground level.

Firstly, we may suppose that the whole atmosphere is subject to turbulence which causes a thorough mixing of the constituents up to the highest levels. In this case the average density ρ at any level h is related to the density ρ_0 at the ground by the equation

$$\rho = \rho_0 \cdot e^{-\frac{h}{H}}$$

where H the height of the homogeneous atmosphere is given by $\frac{RT}{Mg}$, M being the mean molecular weight of air. The calculation is quite simple if the temperature T is constant or if it varies linearly with height. But even if it is not so the calculation can be made graphically if the variation of T with height is known.

Secondly, we may suppose that the atmosphere is not subject to any disturbance. In this case each constituent will be distributed according to Dalton's law, *i.e.*, the density ρ_x of each constituent (x) at any height will be given by

$$\rho_x = \rho x_0 \cdot e^{-\frac{h}{H_x}}$$

where $H_x = \frac{RT}{m_x g}$, m_x being the molecular weight of the constituent (x). The total density at any level will then be given by the sum of the partial densities of the constituents.

Unfortunately, however, neither of these two extreme ideal cases holds good for the entire atmosphere from the ground to the uppermost levels. At the lower levels there is undoubtedly mixing of the various constituents owing to winds and convection currents. At the very high levels, on the other hand, it might be expected that the condition approaches that of diffusion equilibrium under influence of gravity, *i.e.*, the atmospheric constituents are in equilibrium under their own partial pressures according to Dalton's law. In order, therefore, to make an estimate of the proportions in which the atmospheric constituents exist at various levels it is important to know at what level the mixing ceases to be of importance and the diffusive equilibrium begins to predominate.

Besides this there is another factor which further complicates the calculation. Experimental observations show that the nature of the atmospheric constituents in the middle and the upper atmosphere might be different from those in the lower atmosphere. We know now, for instance, that though no trace of oxygen in the atomic state is found in the lower atmosphere spectroscopic study of the polar and non-polar aurora shows that atomic oxygen may be an important constituent in the upper atmosphere.

In order, therefore, to make an estimate of the pressure or density distribution of the various constituents of the upper atmosphere it is necessary to take

into account both these factors. In what follows we will begin by making an estimate of the level above which diffusive equilibrium begins to play the more important part.

DIFFUSION IN THE ATMOSPHERE

All the earlier calculations on the distribution of the atmospheric constituents with height are based on the assumption that the atmosphere, up to the level of the tropopause, is thoroughly mixed and that above this level the atmosphere is free from turbulence.

As a consequence each constituent of the gas above the tropopause was assumed to be distributed according to Dalton's law. This view is now generally held to be incorrect because observations show that winds exist at levels greatly exceeding that of the tropopause.

Now, in order to estimate the diffusion level it is necessary to solve the following important problem. Let the atmospheric gases up to the highest level be thoroughly mixed. If the atmosphere is now left undisturbed how long will it take for the constituent gases to be separated according to Dalton's law by the simultaneous action of diffusion and of gravity? As far as we are aware this problem was first attacked by Maris³ and later by Epstein⁴ following a different method. Results of calculations of both the authors show that equilibrium will set in more rapidly at higher levels where pressure is low than at lower levels where pressure is high. The following table shows some of the results obtained by Epstein :

TABLE I

Time for 50% diffusion.

(After Epstein.)

Height (km.)	He	A	CO ₂
200	2 min.	12 min.	8 min.
180	26 min.	2.3 hrs.	1.6 hrs.
160	4.8 hrs.	25 hrs.	17 hrs.
140	2.8 days	14.8 days	10.4 days
120	34 days	180 days	130 days
100	1.2 years	6.4 years	4.5 years

The question as to the level from which diffusive equilibrium will begin to be important can be settled by observations on the disturbing causes. Assuming that the disturbance occurs periodically we may reasonably take *that* particular level as the height of the commencement of diffusive equilibrium at which the time taken for appreciable separation of the constituents is small compared with the period of the disturbance. Now, observations on meteor trails at heights of 70 or 80 kms. and also on movements of noctilucent clouds between 80 and 100 km. show that these regions are subject to strong winds. Calculations of both Maris and Epstein show, however, that the constituents at this level if once mixed by turbulence will take a long time—measured in years—to settle down to perceptible diffusive equilibrium. We shall therefore not be very wrong if we assume that the lower limit of the level up to which the atmospheric constituents should remain mixed in more or less same proportion as at the surface of the earth cannot be below 100 km.

In order to estimate the upper limit we require the knowledge of the constituents and temperatures in the upper atmosphere and of any periodic disturbance to which it may be subjected.

CONSTITUENTS OF THE UPPER ATMOSPHERE

Our knowledge regarding the constituents in the upper atmosphere is based mainly on spectroscopic studies of the light of the night sky and of polar and non-polar aurora. These give abundant evidence of molecular Nitrogen and atomic Oxygen. Presence of molecular Oxygen is sometimes advocated on the basis of the presence of atomic Oxygen. There is, however, no evidence of atomic Nitrogen. No indication of Helium which is present in definite, though small, amount in the lower atmosphere has yet been found in the upper levels. The existence of atomic Oxygen in large proportion in the upper atmosphere is postulated by the presence of the famous auroral green line λ 5577 with great intensity in the light of the night sky.

The spectroscopic evidence of presence of the auroral green line in the light of the night sky does not necessarily indicate the presence of large proportion of Oxygen in the atomic state. λ 5577 as well as the two other forbidden lines may be excited in the process of dissociation of O_2 . Thus when an O_2^+ ion captures an electron its constituent atoms will be raised to excited states and the O_2 molecule may dissociate giving $O(^1D_0)$ or $O(^1S_0)$. These excited atoms will produce the red and the green auroral lines. Again neutral O_2 molecule will dissociate by absorption of radiation of wavelength $<\lambda$ 1750. One of the dissociated products is Oxygen atom in the excited D state which will give rise to λ 5577. Thus it is seen that the presence of Oxygen in molecular form rather than in atomic form is necessary for the production of λ 5577 because according

to the above view the excited D- and P-states of atomic Oxygen which are essential for the production of the auroral lines can only be obtained directly from the O_2 molecules.

The presence of O_2 rather than O in the upper atmosphere is also supported by observations on the auroral spectrum. This spectrum, as is well-known, has strong negative bands due to N_2^+ . If the upper atmosphere consists of N_2 and O_2 then, if diffusive equilibrium sets in N_2 will be the major constituent in the uppermost regions which are the first to receive electronic bombardment for producing the aurora.

It should, however, be mentioned that alternative hypotheses have been put forward from time to time to explain the emission of the auroral lines directly from atomic Oxygen. For instance, Martyn and Pulley⁵ think that the electron which escapes when O^+ combines with O to form O_2 may collide with an Oxygen atom and raise it to an excited metastable state. The probability of excitation by such electronic collision is not very large. In fact electronic collision, in order to be efficient for excitation, must not possess energy much larger than that necessary for the excitation. The escaped electron as described by Martyn and Pulley, possesses about 4 volts energy whereas the energy needed for raising normal atom in the P-state to the metastable S-state is 3.4 volts. Consideration of the auroral spectrum also leads one to the same conclusion: This spectrum which is believed to be produced by electronic bombardment gives the λ 5577 line very much weaker than the negative bands of Nitrogen.

Another hypothesis regarding the production of the forbidden lines from atomic Oxygen may also be mentioned. According to A. K. Das⁶ the forbidden lines may be regarded as due to fluorescence of the Oxygen atoms under the influence of dilute radiation. The forbidden lines being not resonance lines cannot directly absorb energy of the corresponding wavelengths from the solar spectrum. Atomic Oxygen may, however, by direct absorption be raised to higher excited states and from these states drop to the metastable S- and D-states. According to Das the excited atoms by inelastic collision with neutral molecules produce increase of temperature of the upper atmosphere.

In view of the above discussion regarding the constituents in the upper atmosphere it seems that the presence of neither O_2 nor O can be ignored. We have, therefore, worked out the distribution for the two cases, namely, for the upper atmosphere consisting of (i) N_2 and O and (ii) N_2 and O_2 .

TEMPERATURE IN THE UPPER ATMOSPHERE

Regarding the temperature above 100 km. it is now believed to be much higher in the F region than in the E region. For example the observed diurnal and seasonal variation of the ionisation density of the E region can be explained

if a high temperature of about 1200°K to 1500°K is assumed in the daytime. Again interferometer study of the width of the $\lambda 5577$ auroral green line tells us that the emitting Oxygen atoms must have average velocity corresponding to a temperature of about 2000°K . Further, Helium which is known to exist in the lower levels of the atmosphere and which is being continually emanated from the helium fields of North America cannot be detected either in the light of the night sky or in the auroral spectrum. This can be explained if it is assumed that owing to high temperature ($\approx 1200^{\circ}\text{K}$) existing in the upper atmosphere the helium atoms attain such high velocities that they overcome the earth's gravitational pull and are therefore continually escaping from the earth's atmosphere. In our calculations, therefore, we have assumed that the temperature starting from 300°K at 100 km. rises linearly with height at the rate of 4°K per km. reaching a value of 1100°K at 300 km.

DISTURBANCE IN THE UPPER ATMOSPHERE

Regarding the disturbances it has been more or less established by radio observations that the whole of the upper atmosphere beginning from the E-layer is subject to both diurnal and seasonal heating and cooling, *i.e.*, to expansion and contraction. We may, therefore, take the level of diffusion as that height at which the time required for perceptible separation by diffusion is much less than the period of heating and cooling, *i.e.*, twenty-four hours. In round figures we will take this time to be 10 hours. It is thus seen that the results of calculations of the diffusion levels made by Maris and by Epstein cannot be utilised in the upper atmosphere above 100 km. Because neither of these authors takes into account the possibility either of the existence of any constituent in the upper atmosphere which is not found near the ground level, or of the disturbing effect of periodic heating and cooling. Moreover the analysis of Maris contains several assumptions which cannot properly be justified. Epstein's analysis, on the other hand, is not applicable in our case because he has studied the diffusion of gases which are present only in small quantities in the atmosphere, so that the density distribution of the atmosphere is not sensibly influenced by diffusion separation. In addition, both Maris and Epstein have assumed a constant temperature throughout the entire atmosphere.

HEIGHT OF DIFFUSION LEVEL

We shall now proceed to find the diffusion level first on the assumption that the upper atmosphere consists of molecular Nitrogen and atomic Oxygen. In order to do this we require a knowledge of the pressure and the composition at some datum level. This datum level we will take to be 100 km. which, as we

have seen, may be taken as the lower limit of the level up to which thorough mixing may be assumed to have extended from the ground. The pressure at this level is now known with some certainty to be 10^{-3} mm. and temperature 300°K. These are obtained both from radio observations of collisional frequency of electrons with neutral gas molecules and atoms in the E region and also from calculations made by making certain very plausible temperature distribution.⁵

The pressure and temperature at the datum level being known the composition may be worked out. If the constituent gases were N_2 and O_2 in approximately the same proportion as near the ground level then the respective numbers of molecules per c.c. would be 2.543×10^{13} and 6.963×10^{12} . As mentioned before we will first work out the distribution assuming that below 100 km. the constituent gases are N_2 and O_2 but that above this level they are N_2 and O. We can make an estimate of the respective numbers per c.c. of N_2 and O just above 100 km. from the consideration that all the O_2 molecules are dissociated into O atoms. This would entail an increase in the total number of particles per c.c. by 21.5% causing an increase of pressure. In order to maintain the continuity of pressure across the surface of separation at the 100 km. level we imagine the excess of Oxygen atoms tending to cause an increase of pressure to have drifted upward such that the number of N_2 molecules per c.c. at this level is still 2.543×10^{13} and that of O atoms per c.c. is 6.963×10^{12} . This assumption also maintains that the total number of N_2 molecules above 100 km. is the same after dissociation of O_2 as before and that the total number of O atoms above this level is twice that of O_2 molecules above this level before these were dissociated. Actually, of course, the change-over of the constituent gases takes place gradually and there should, in effect, be an intermediate region where N_2 , O_2 and O are simultaneously present.

With these assumptions regarding the conditions and composition at the datum level and the temperature distribution in the upper atmosphere we proceed as follows. We first find the time taken by the constituent gases of a thoroughly mixed atmosphere of two gases to be separated according to Dalton's law by the simultaneous action of diffusion and of gravity.

The number of molecules $(N_1)_D^\uparrow$ of gas (1) diffusing upward in unit time across one sq. cm. of horizontal plane at level z above the datum level is given by

$$(N_1)_D^\uparrow = -D \frac{\partial n_1}{\partial z}, \quad (1)$$

where n_1 is the molecular density of gas (1) at level z and D is the coefficient of diffusion given by

$$D = \frac{1}{3} \cdot \frac{n_1 \lambda_2 c_2 + n_2 \lambda_1 c_1}{n_1 + n_2}, \quad \dots (2)$$

where n_1 and n_2 are the molecular densities of the two gases, λ_1, λ_2 are their mean free paths and $\bar{c}_1, \bar{c}_2$ are their mean molecular velocities, all these quantities being referred to the level z .

The molecules of gas (1) will simultaneously experience a steady downward velocity due to gravity. If this be v_1 then the number of molecules of gas (1) coming down across one sq. cm. in unit time is given by

$$(N_1)_z \downarrow = v_1 n_1 \quad \dots (3)$$

The total number of molecules going upward across one sq. cm. in unit time is therefore

$$(N_1)_z \uparrow = -D \frac{\partial n_{1z}}{\partial z} - v_1 n_1 \quad \dots (4)$$

In the case of a linear gradient of temperature, as we have assumed, the total number of molecules $n_z (= n_{1z} + n_{2z})$ per c.c. under the condition of thorough mixing at level z is given by

$$\begin{aligned} n_z &= \frac{n_0}{1 + \alpha z} \cdot e^{-\frac{gM}{R} \int_0^z \frac{dz}{T_z}} \\ &= \frac{n_0}{1 + \alpha z} \cdot e^{-\frac{gM}{R} \int_0^z \frac{dz}{T_0(1 + \alpha z)}} \\ &= n_0 (1 + \alpha z)^{-1 - \frac{gM}{\alpha T_0 R}} \quad \dots (5) \end{aligned}$$

where n_0 is the total number of molecules per c.c. at datum level,

g is the acceleration due to gravity at level z which we assume to be the same as at ground level,

M is the mean molecular weight of the gas with composition as at the datum level,

R is the universal gas constant,

T_0 is the temperature at the datum level = 300°K,

α is the coefficient of increase of temperature with height above datum level = $\frac{4}{3} \times 10^{-7}$ degree/cm./deg, in our case.

When equilibrium is attained under the joint action of diffusion and gravity we have

$$N_{1z} = 0$$

$$n_{1z} = n_{10} (1 + \alpha z)^{-\frac{gM_1 + \alpha' T_0 R}{\alpha' T_0 R}} \text{ and } n_{2z} = n_{20} (1 + \alpha z)^{-\frac{gM_2}{\alpha' T_0 R}} \quad (6)$$

M_1 and M_2 being the molecular weights of the constituents (1) and (2).

Substituting appropriate values in equation (4) we find, for equilibrium condition,

$$0 = D \cdot \frac{gM_1 + \alpha' T_0 R}{RT_z} \cdot n_{1z} - v_1 n_{1z}$$

or
$$v_1 = D \cdot \frac{gM_1 + \alpha' T_0 R}{RT_z}$$

Equation (4) may therefore be written in the form

$$(N_{1z})' = -D \left(-\frac{\partial n_{1z}}{\partial z} + \frac{gM_1 + \alpha' T_0 R}{RT_z} \cdot n_{1z} \right) \quad (8)$$

It is obvious that with the progress of separation by diffusion and gravity, n_{1z} , n_{2z} , λ_{1z} , λ_{2z} , $\frac{\partial n_{1z}}{\partial z}$, $\frac{\partial n_{2z}}{\partial z}$ are all changing and hence the nature of the variation of N_1 (or N_2) with diffusion separation as given by equation (8) is very complicated and beyond our present knowledge. An approximate solution has, therefore, been attempted on the following line.

Let us call the fractional diffusion at any stage of diffusion to be η . Then η is the ratio of the total number of molecules of gas (1) [or (2)] that have gone upward at any stage of diffusion to the total number of molecules of the same gas that must go upward for complete equilibrium. Then since N_{1z} and hence n_{1z} and $\frac{\partial n_{1z}}{\partial z}$ depend upon η and *vice versa* we may assume

$$(n_{1z})_\eta = (n_{1z})_{\eta=0} \cdot e^{-\beta_1 \eta},$$

$$\left(\frac{\partial n_{1z}}{\partial z} \right)_\eta = \left(\frac{\partial n_{1z}}{\partial z} \right)_{\eta=0} \cdot e^{-\theta_1 \eta},$$

and similarly for gas (2).

It is evident that η varies from 0 at the beginning to 1 at equilibrium condition. From boundary conditions the values of β_1 and θ_1 and also of β_2 and θ_2 are easily determined. For example, to evaluate β_1 we have

$$(n_{1z})_{\eta=1} = (n_{1z})_{\eta=0} e^{-\beta_1}$$

$$\text{or } n_{10}(1+az)^{-\frac{gM_1}{\alpha T_0 R} - 1} = n_{10}(1+az)^{-\frac{gM}{\alpha T_0 R} - 1} e^{-\beta_1}$$

$$\text{or } e^{-\beta_1} = (1+az)^{-\frac{g}{\alpha T_0 R}(M_1 - M)}$$

$$\text{In the same way } e^{-\theta_1} = \frac{gM_1 + \alpha T_0 R}{gM + \alpha T_0 R} e^{-\beta_1}.$$

Having found β_1 , β_2 , θ_1 and θ_2 the values of n_1 , n_2 , λ_1 , λ_2 , $\frac{\partial n_1}{\partial z}$, $\frac{\partial n_2}{\partial z}$ are all found out and hence the rate of separation N_{1z} is determined for any stage of diffusion.

To find out the time required for a certain percentage of diffusion we take recourse to graphical integration. The variation of η from 0 to 1 is divided into equal intervals of 0.1 and the values of N_{1z} for $\eta=0$, $\eta=0.1$, $\eta=0.2$, etc., are calculated. The values of N_{1z} for $\eta=0$ and for $\eta=0.1$ give us the mean value of N_{1z} for the interval $\eta=0$ to $\eta=0.1$, i.e., for the first 10% diffusion. Now the total number of molecules of gas (1) to be separated for complete diffusion is given by

$$X_{1z} = \left[(p_{1z})_{\eta=0} - (p_{1z})_{\eta=1} \right] \times \text{total number of molecules of gas (1) to produce unit pressure,}$$

where p_{1z} is the partial pressure of gas (1) at level z and hence the time for the first 10% diffusion is easily calculated. Similarly, the times for the successive 10% diffusions are found out. The total time required for some 80% diffusion is then calculated for various levels. Table II gives the results for some typical cases, the heights being reckoned from the ground level. Column 1 gives the times for an upper atmosphere consisting of N_2 and O and having a rising temperature as assumed above.

Similar calculations are made for an upper atmosphere consisting of N_2 and O_2 . Column 2, Table II, gives the results on the assumption of a gradually rising temperature as in the case considered above and Column 3 gives the results for a constant temperature of 300°K above 100 km.

TABLE II
Time for 80% diffusion.

Height (km.).	N ₂ , O Rising temperature.	N ₂ , O ₂ Rising temperature.	N ₂ , O ₂ Constant temperature.
105	...	...	14.12 hours.
175	..	68.26 hours	5.53 ..
200	...	...	0.46 ..
225	...	10.09 ..	..
250	17.47 hours	3.9 ..	...
300	7.98 ..	...	...
350	3.67 ..	..	...

It will be seen that on the assumption of the upper atmosphere consisting of N₂ and O and of a linear increase of temperature with height above 100 km. the time for 80% diffusion at 350 km. above the ground is 3.67 hours. The constituents may therefore be assumed to be in diffusive equilibrium above this level. It is also found that at a height of 175 km. there is only about 30% diffusion in 10 hours and consequently the constituents may be taken as more or less completely mixed up below this level. In the intermediate region between 175 km. and 350 km. there is only partial mixing.

If the constituents in the upper atmosphere are assumed to be N₂ and O₂ then the corresponding levels are 250 km. and 175 km. respectively on the assumption of a rising temperature and 175 km. and 150 km. for a constant temperature 300°K.

TABLE III
Percentage diffusion at various levels after 10 hours.
(Linear gradient of temperature.)

Height (km)	N ₂ , O	N ₂ , O ₂
100	0	0
125	3.5%	2.5%
150	10.5 ..	9 ..
200	43 ..	47 ..
250	71 ..	95 ..
300	83 ..	practically
350	91 ..	complete
400	...	equilibrium

Table III gives the percentage of diffusion at the various levels when diffusion has progressed for 10 hours. The composition and pressure at this time at the various levels are then easily calculated from the knowledge of the corresponding percentage of diffusion. Tables IV and V give the partial and total pressures at and amounts of gas at N. T. P. above the different levels. It may be remarked that these values are higher than those obtained by previous workers.

It is certainly interesting to note that if the constituent gasses are N_2 and O and a rising temperature is assumed then the total pressure at a height of 250 km. (average F layer height) is 6×10^{-7} mm. On the classical theory this would correspond to a collisional frequency $\nu = 7.4 \times 10^2$ of electrons with neutral gas molecules and atoms. This agrees fairly well with that (1.5×10^3) obtained for the F region by radio methods.

TABLE IV

Partial and total pressures at and amount of gas above different levels.
Composition— N_2 , O; rising temperature.

Height (km.)	Partial pressures (mm.)		Total pressure (mm.)	Amount of gas (cm.) at N.T.P.	
	N_2	O		N_2	O
100	7.85×10^{-4}	2.15×10^{-4}	1.00×10^{-3}	0.85	0.41
125	8.96×10^{-5}	2.54×10^{-5}	1.15×10^{-4}	9.76×10^{-2}	4.84×10^{-2}
150	1.62×10^{-5}	5.35×10^{-6}	2.16×10^{-5}	1.76×10^{-2}	1.02×10^{-2}
200	1.02×10^{-6}	1.03×10^{-6}	2.05×10^{-6}	1.11×10^{-3}	1.97×10^{-3}
250	1.14×10^{-7}	4.89×10^{-7}	6.03×10^{-7}	1.24×10^{-4}	9.33×10^{-4}
300	2.02×10^{-8}	2.45×10^{-7}	2.65×10^{-7}	2.20×10^{-5}	4.67×10^{-4}
350	4.73×10^{-9}	1.47×10^{-7}	1.52×10^{-7}	5.14×10^{-6}	2.80×10^{-4}
400	1.31×10^{-8}	1.08×10^{-7}	1.09×10^{-7}	1.42×10^{-6}	2.06×10^{-4}

CONCLUSION

It is seen that if the disturbing causes due to winds in the middle atmosphere and due to periodic heating and cooling in the upper atmosphere are taken into account, diffusive equilibrium of the constituent gases begins to be important only at great heights.

TABLE V

Partial and total pressures at and amount of gas above different levels.
Composition— N_2 , O_2 ; rising temperature

Height (km.)	Partial pressures (mm.)		Total pressure (mm.)	Amount of gas (cm.) at N.T.P.	
	N_2	O_2		N_2	O_2
100	7.85×10^{-4}	2.15×10^{-4}	1.00×10^{-3}	85	0.20
125	6.79×10^{-5}	1.81×10^{-5}	8.63×10^{-5}	7.38×10^{-2}	1.75×10^{-2}
150	1.02×10^{-6}	2.66×10^{-6}	1.20×10^{-5}	1.11×10^{-2}	2.53×10^{-3}
200	6.37×10^{-7}	1.10×10^{-7}	7.47×10^{-7}	6.97×10^{-4}	1.05×10^{-4}
250	8.81×10^{-8}	7.11×10^{-9}	9.52×10^{-8}	9.58×10^{-5}	6.77×10^{-6}
300	1.70×10^{-8}	1.02×10^{-9}	1.80×10^{-8}	1.85×10^{-5}	9.71×10^{-7}
350	4.28×10^{-9}	2.10×10^{-10}	4.49×10^{-9}	4.65×10^{-6}	2.00×10^{-7}
400	1.31×10^{-9}	5.42×10^{-11}	1.36×10^{-9}	1.42×10^{-6}	5.16×10^{-8}

It is also found that the pressures at and the amounts of the constituent gases above different levels in the upper atmosphere are higher than those obtained by previous workers.

Our calculations show that if the upper atmosphere consists of N_2 and O then the region above 250 km. will consist largely of Oxygen atoms. As mentioned before this seems to contradict the results of observation on high altitude auroral spectra which show a greater intensity of the negative bands of Nitrogen.

Study of the decay of the night time ionisation of the F region of the Ionosphere also shows that it is highly improbable that the upper atmosphere should consist of atomic Oxygen. Oxygen in the atomic state is believed to have strong affinity for electrons. It may be shown that if the upper atmosphere consisted entirely of Oxygen atoms then the electrons would disappear by attachment very quickly. Since, however, F region ionisation is known to persist throughout the whole night it may not be improbable that the constituents of the upper atmosphere are N_2 and O_2 rather than N_2 and O .

In conclusion, we have much pleasure in acknowledging our thanks to Mr. S. B. Bandyopadhyaya, M. Sc., for his help in preparing the tables.

R E F E R E N C E S

- ¹ Wegener, *Thermodynamik der Atmosphäre* (1911).
- ² Chapman and Mihne, *Q. J. Roy. Met. Soc.*, **46**, 357 (1920).
- ³ Maris, *Ferr. Mag.*, **33**, 293 (1928) ; **34**, 45 (1929).
- ⁴ Epstein, *Gerl. Beitr. z. Geophys.*, **35**, 153 (1932).
- ⁵ Martyn and Pulley, *Proc. Roy. Soc.*, **154**, 455 (1936).
- ⁶ Das, *Gerl. Beitr. z. Geophys.*, **40**, 241 (1937).

WIRELESS LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE,
9-22 UPPER CIRCULAR ROAD,
CALCUTTA.

THE CONSTITUTION OF HEAVY WATER

By I. RAMAKRISHNA RAO, M.A., PH D., D.Sc.

AND

P. KOTESWARAM, B.Sc. (HONS.)

Andhra University, Waltair

(Received for publication, February 18, 1938.)

ABSTRACT. The Raman band of heavy water is found to be similar to that of ordinary water both in diffuseness and extent. The variations with temperature in the structure of this band are also similar to those of ordinary water. These changes are attributed to changes in the relative proportions of D_2O , $(D_2O)_2$ and $(D_2O)_3$ molecules which are assumed to be in thermal equilibrium. By an analysis of the intensity curves of the band, the proportions of the three polymers at different temperatures are calculated. The results are compared with those of water and the points of similarity and differences explained on the basis of their other physical properties.

1. INTRODUCTION

Soon after the discovery of heavy water, Wood¹ studied its Raman spectrum and found that it gives rise to a broad and diffuse band with a maximum of intensity having Raman frequency equal to 2517 cm^{-1} . Later Ananthakrishnan² reported that in addition to the principal band which actually consists of three components with frequencies 2363 , 2515 and 2662 cm^{-1} there are two comparatively fainter bands at 1110 and 1250 cm^{-1} . Bauer and Magat,³ however, found only two components in the principal band at 2389 and 2509 cm^{-1} . The other bands reported by them are at 170 , 350 , 500 and 1207 cm^{-1} , the one at 1110 found by Ananthakrishnan not being observed in their spectra. Rank, Larson and Bordner⁴ studied the Raman spectrum of D_2O in the vapour state, which revealed a comparatively sharp line at 2666 . On account of the similarity in the general features of the Raman spectra of D_2O outlined above and those of water extensively investigated by a number of workers, we undertook a study of D_2O on lines similar to the work⁵ of one of us on water in its various phases. The results reveal not only certain points of resemblance in general, but some interesting differences in detail which are described in the succeeding parts of this communication.

2. EXPERIMENTAL TECHNIQUE

Since the D_2O available to us was small in quantity, it was found necessary to adopt an arrangement by which wastage of the substance is avoided as far as possible, particularly during our study at the higher temperatures where loss due to evaporation may be considerable. Hence the heavy water was kept in a tube sealed under vacuum. This procedure was necessary for other considerations also. The sample supplied by Norsk Hydro-Electric Company when studied directly gave a strong continuous background in the Raman spectrum, possibly due to slight traces of fluorescent impurities. It was therefore found necessary to distil it in vacuum. On account of certain convenient features in the arrangement which may be adopted for investigation of similar substances, the details of the technique are briefly outlined in figure 1.

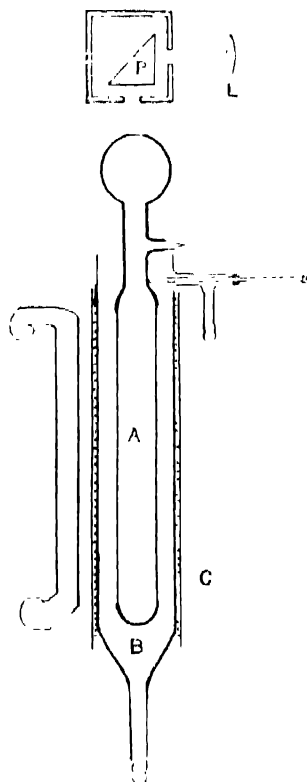


FIGURE 1

The glass tube A, 2 cm. in diameter, is 15 cm. long and has a narrow stem at the top at the end of which is blown a spherical bulb with its surface as clear as possible. The bottom of the tube is closed and the side tube indicated in the diagram is connected to another bulb not shown in the figure. After pouring the D_2O in this bulb, it is exhausted and sealed. After repeated distillation of

heavy water into A, the side tube is sealed off at the constriction previously provided. It is placed vertically in an outer jacket B through which water is circulated. This is surrounded by a heating coil which is protected from the atmosphere by the glass tube C. A vertical type of mercury arc is placed as near as possible to the outermost jacket C. The tube A, containing heavy water up to the side tube, is painted black all over leaving a clear portion at the centre for the liquid column to be exposed to the mercury arc light. A small circular clear space is provided at the top of the bulb to transmit the scattered radiation which after total reflection through the right-angled prism P is concentrated on to the slit of the spectrograph by the achromatic lens L. The current through the coil is so adjusted and the water circulated through B so regulated that a steady desired temperature is reached. The temperature of the circulating water was noted by a thermometer introduced through the side tube and after it was steady for a considerable period, the spectrum of the scattered radiation was taken. The narrow tube at the top of A served the purpose of a diaphragm to cut off parasitic light from the sides of the tube. The bottom of A and the surface of the liquid layer were protected from the direct mercury arc light to eliminate the intense scattering from them.

For temperatures lower than that of the laboratory, the tube containing heavy water is dipped in a transparent thermos flask containing cold water, which is kept at a constant temperature by adding ice and stirring.

3 STRUCTURE OF THE D_2O AND H_2O BANDS

The Raman spectrum of heavy water reveals a broad diffuse band as for ordinary water, with three clear maxima having Raman frequencies equal to 2394, 2534 and 2674 cm^{-1} . The following table contains the frequencies as given by different authors on this band :—

TABLE I
Raman frequencies of the D_2O band

Author.	Raman frequencies of maxima.		
Wood	—	2517	—
Ananthakrishnan	2358	2507	2680
Bauer and Magat	2389	2509	—
Authors	2394	2534	2674

Except for slight differences in the frequencies of maxima there is general agreement as to the existence of at least two components in the band. Wood used the $2537\text{\AA}$ line of the mercury arc for exciting the band and might have measured its wavelength by a micrometer, which gives only an approximate value on account of the diffuseness of the band. The other two sets of values for excitation by the $4047\text{\AA}$ line are also the result of micrometric measurements. In a case like this where a spectral line is very diffuse it is always desirable to take a microphotometric curve for finding the exact position of the maxima. This is what we have done and the values given by us are the result of such a measurement.

By a study of the D_2O band at different temperatures which will be described in detail later, we found large variation in the relative intensities of the three components, the one of lower frequency increasing in intensity with diminishing temperature, the highest frequency component at the same time diminishing in intensity, the central component remaining approximately constant. This explains the absence of the third frequency in Bauer and Magat's results as the temperature of their laboratory must have been much lower than that of the tropical laboratories where Ananthakrishnan and the authors work. This discrepancy should not therefore be taken as a genuine difference in the structure of the bands as was the case with water. In the later, there was controversy for a long time as to whether Raman band of water consists of three or two components, the continental workers finding only two clear maxima, while the workers in India observed a third faint component. In a work of this kind where variation in the structure varies considerably with temperature, it is therefore always desirable to make note of the temperature at which the investigation is carried.

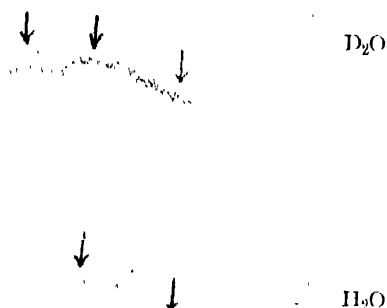


FIGURE 2

Before giving our results with variation in the structure of the D_2O band with temperature, a comparative study of the microphotometric curves of this band and that for H_2O at the same temperature, are given below. Both the bands are very broad and diffuse. While the H_2O band extends from about 5052 cm^{-1} to 3834 cm^{-1} , a range of about 782 wave numbers, that of D_2O ranges from 2254 to 2784 cm^{-1} with a width of 530 wave numbers. This indicates that the width of the D_2O band is decidedly smaller than that of H_2O . For a comparison of the two bands, their microphotometric curves are given in figure 2.

While there is a significant similarity in the two curves with regard to diffuseness and structure, there is a fundamental difference in their extent and relative intensities of the components. The extent of the D_2O curve in the figure is decidedly smaller than that of H_2O . This disparity in the extent of the two bands is actually greater than what is recorded in the figure on account of the lower dispersion of the prism spectrograph in the region where the H_2O band falls. It is also clear from the curves that for heavy water, the components (marked with arrows) are better resolved, the first component with $\Delta\nu = 2394\text{ cm}^{-1}$ being of the same intensity as the second, whereas for ordinary water, the first component is not only not well resolved from the second, but is also less intense.

4. STRUCTURAL VARIATION OF THE D_2O BAND WITH TEMPERATURE

On account of the close similarity in the nature of the D_2O and H_2O bands, we investigated the structure of the D_2O band at 6, 30, 65 and 100°C on lines similar to the work on H_2O by one of us.⁶ The microphotometric curves of the Raman band for D_2O at different temperatures are taken and the intensities at different points on the bands are calculated by the usual method. The results are given in table II, in which the intensities against the corresponding frequencies are recorded for the four different temperatures.

For a clear understanding of the variations in the structure of the band with temperature, the results in table II are graphically represented in figure 3, with the frequencies along the abscissa and the corresponding intensities along the ordinate.

TABLE II.

Intensity distribution of the Raman band of D₂O at different temperatures

6°C.		30°C.		65°C.		100°C.	
$\Delta\nu$ in cm^{-1}	Int.	$\Delta\nu$ in cm^{-1}	Int.	$\Delta\nu$ in cm^{-1}	Int.	$\Delta\nu$ in cm^{-1}	Int.
2254	0	2254	0	2254	0	2254	0
2314	16.7	2314	4.0	2314	0.9	2314	2.6
2354	10.4	2354	16.8	2354	18.3	2354	0.2
2374	20.6	2374	18.3	2390	18.1	2390	7.0
2390	15.5	2390	21.4	2404	18.1	2424	10.9
2412	14.4	2404	21.1	2500	20.4	2470	14.7
2434	16.3	2420	18.5	2515	20.6	2514	19.0
2439	16.7	2434	15.1	2591	15.7	2545	19.6
2580	11.8	2470	18.3	2674	9.7	2580	14.9
2630	9.9	2484	21.4	2690	9.7	2630	5.2
2690	3.9	2534	22.2	2720	1.8	2660	6.1
2750	0.6	2564	20.2	2750	1.7	2674	11.6
2784	0	2630	12.5	2784	0	2690	15.2
		2660	11.6			2720	4.8
		2704	6.3			2784	2.2
		2784	0			2800	0

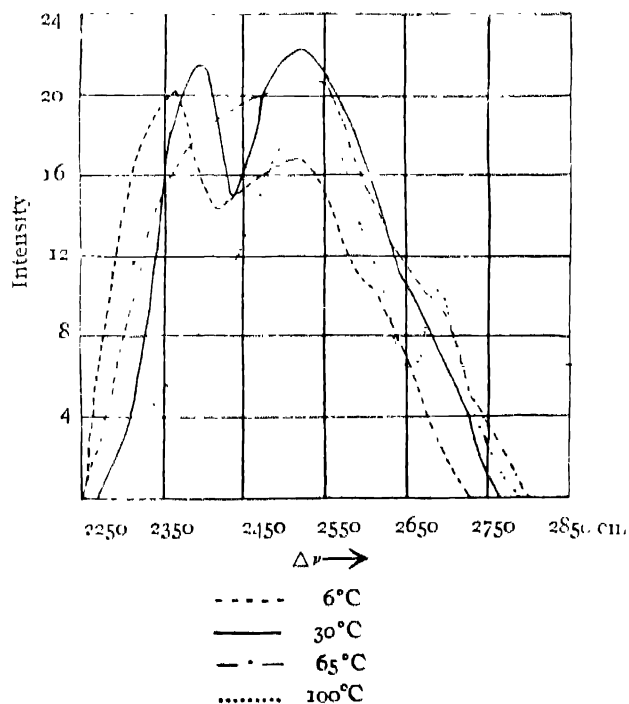


FIGURE 3

The extent of the band is almost the same for all temperatures, but the variations in the distribution of intensity from one temperature to another are very conspicuous. While the intensity curve for 6°C shows two clear maxima at 2365 and 2530 with an inflection at 2615 cm^{-1} , that for 30°C contains the maxima and inflection at 2395, 2535 and 2655 cm^{-1} respectively. At 60°C there is only one clear maximum at 2550 cm^{-1} with a small inflection at 2695 cm^{-1} , while at 100°C again there are two well defined maxima at 2540 and 2690 cm^{-1} with an inflection at 2350 cm^{-1} .

It is evident from the above observations that the clear maximum of lowest frequency at about 2395 cm^{-1} , changes very rapidly in intensity with increasing temperature, the frequency changes, however, being negligible and within the order of accuracy with which they can be determined. This maximum which is most intense at 6°C is reduced to almost equal intensity with the second at 30°C diminishing further at 60°C and almost disappearing at 100°C, excepting for a small inflection in the curve for this temperature.

The central maximum, however, persists with equal intensity at all temperatures. The third maximum which makes its appearance clearly at 100°C with a frequency equal to 2690 cm^{-1} is perceptible, at other temperatures as a mere inflection, the prominence of this inflection diminishing with falling temperature.

5. EXPLANATION OF THE ABOVE RESULTS.

The close resemblance between the D_2O and H_2O Raman bands, not only in their diffuseness and structure, but also in respect of changes in the distribution of intensity in the bands with temperature, leads naturally to the conclusion that the explanation given by one of us⁷ for these phenomena in H_2O applies equally well to the case of D_2O . The three components in the H_2O bands were attributed to three polymers of water, H_2O , $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ and the changes in the relative intensities of these components were explained as arising out of changes in the relative proportions of these polymers with temperature. The arguments put forward by some authors against this hypothesis were fully dealt with in another paper.⁸ The hypothesis of the existence of polymers in water is not a new one and the explanation of the above phenomena for H_2O on this hypothesis is so natural that it is extended to the case of D_2O as well, which is its isotopic analogue.

By studying the Raman spectrum of D_2O vapour, Rank, Larson and Bordner found a single line at 2666 cm^{-1} similar to the single line in H_2O vapour at 3650 cm^{-1} . This indicates that in the vapour state heavy water consists entirely of single molecules. The component in nearly the same position (2690 cm^{-1}) for this substance in the liquid state at 100°C is therefore attributed to D_2O molecules, the other two components of smaller frequencies in the band

being assigned to $(D_2O)_2$ and $(D_2O)_3$ molecules as in the case of ordinary water.

The diminution with increasing temperature in the intensity of the 2394 cm^{-1} component, attributed to the $(D_2O)_3$ molecules, is explained as due to diminution in the proportion of these molecules which with increasing temperature change to the other polymers. The increasing intensity of the third component 2690 cm^{-1} with increasing temperature is ascribed to the increasing proportion of the single molecules to which this component is assigned. The approximate constancy in the intensity of the central component 2534 cm^{-1} is taken as an indication that the proportion of the double molecules giving rise to this component is nearly constant. This is also taken as indicating the comparatively greater stability of the double molecules.

It would have been interesting to study the Raman spectrum of heavy ice, but on account of the difficulty in maintaining it in the solid condition at a steady temperature, the work could not be undertaken.

6. RELATIVE PROPORTIONS OF THE POLYMERS IN HEAVY WATER

With a view to determine roughly the relative proportions of the three polymers in heavy water at different temperatures, the intensity curves of the heavy water band are analysed on lines similar to the analysis of the corresponding curves for ordinary water.⁹ The curves for 6, 30, 65 and 100°C as analysed are given in figures 4, 5, 6 and 7 respectively.

In table III are collected the frequencies of the positions of maxima and extents of the three components of the curves as obtained by the analysis.

TABLE III.

Frequencies of maxima and extent of the D_2O , $(D_2O)_2$
and $(D_2O)_3$ Components

Temp.	$(D_2O)_3$ component.		$(D_2O)_2$ component.		D_2O component.	
	Position of Max ^m .	Extent.	Position of Max ^m .	Extent.	Position of Max ^m .	Extent.
6°C .	2365	2254-2540	2530	2413-2645	2645	2575-2725
30°C .	2395	2270-2535	2535	2430-2645	2640	2535-2765
65°C .	2400	2254-2535	2545	2400-2700	2695	2550-2785
100°C .	2420	2295-2535	2540	2420-2650	2690	2590-2800

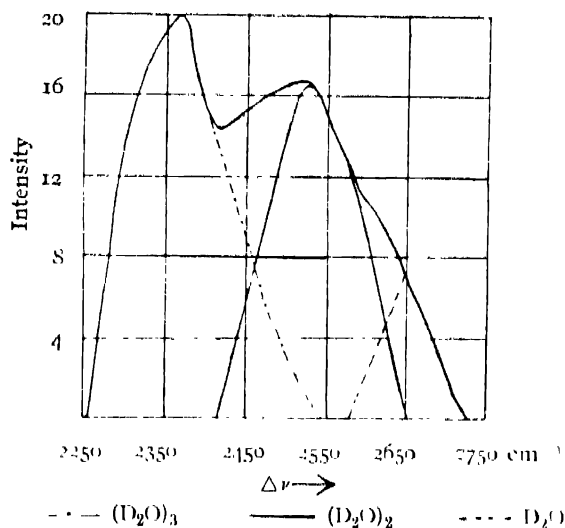


FIGURE 4.

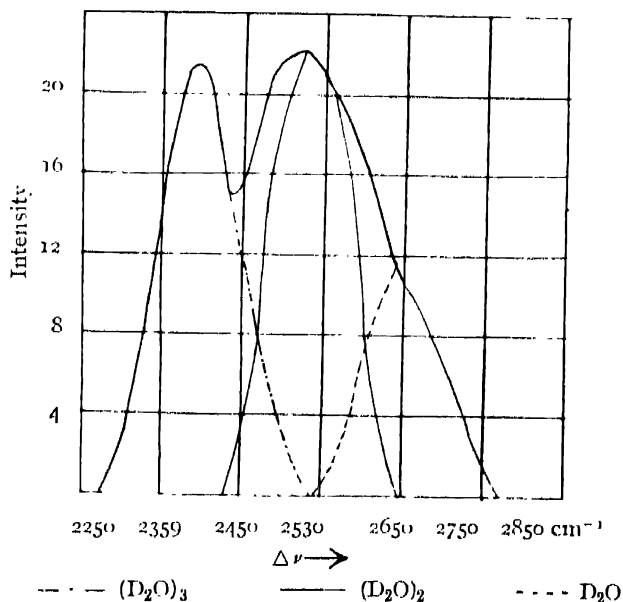


FIGURE 5

Considering the roughness of the analysis, it can be asserted from the table that the maxima and extent of the components are very nearly constant.

On the supposition that the probability of excitation of the three polymers is the same and that the contribution to the intensity of the band by the D_2O molecules is the same as that of the $(D_2O)_2$ or $(D_2O)_3$, the relative intensities of the components are assumed to be proportional to the relative number of the polymerised molecules, as was done for water. This is justifiable by the fact that a quantum of light incident upon a group of molecules can excite either the

internal oscillations of one of the constituent molecules, or the external oscillations between one molecule, and another of the same group, but cannot excite the internal oscillations of all the molecules lying in a single group. Also, the probability of three different quanta, exciting the three different constituent molecules in a group at one and the same time is bound to be negligibly small.

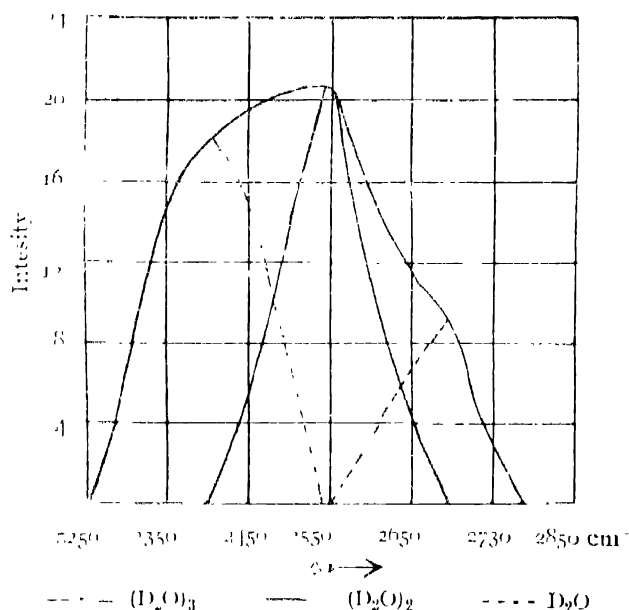


FIGURE 6

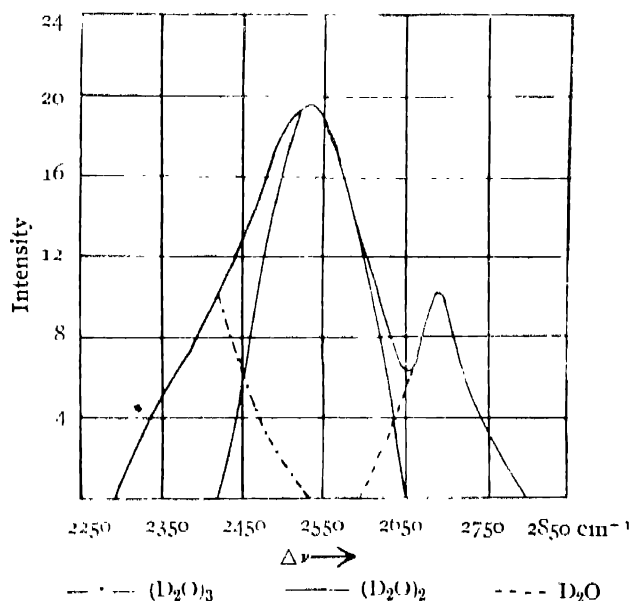


FIGURE 7

Since the extents of the three components are nearly the same, the ratio of the heights of their peaks, are assumed to give the direct ratio of the three polymers. The relative proportions of the polymers as calculated by this method are given in table IV.

TABLE IV
Relative proportions of D_2O , $(D_2O)_2$ and $(D_2O)_3$ in heavy water
at different temperatures

Temp.	Relative intensity.			Percentage by numbers.			Percentage by weight.		
	$(D_2O)_3$	$(D_2O)_2$	D_2O	$(D_2O)_3$	$(D_2O)_2$	D_2O	$(D_2O)_3$	$(D_2O)_2$	D_2O
6°C	20	16.5	7	46	38	16	60	33	7
30°C	20.4	21	11.2	39	41	20	53	37	10
65°C	18	20.6	9	38	42	20	52	39	11
100°C	10	19.5	12	21	48	28	37	49	14

It is evident from the above table that while the percentage of the triple molecules is nearly halved and of the single molecules nearly doubled from the lowest to the highest temperature, the change in the double molecules is comparatively small. These changes are similar to those in ordinary water. For comparison the proportions for ordinary water taken from a previous paper¹⁰ of one of us are given in table V.

TABLE V
Relative proportions of $(H_2O)_3$, $(H_2O)_2$ and H_2O molecules in water at
different temperatures

Temp.	Percentage by numbers.			Percentage by weight.		
	$(H_2O)_3$	$(H_2O)_2$	H_2O	$(H_2O)_3$	$(H_2O)_2$	H_2O
9°C	23	58	19	34	57	9
4°C	22	58.5	19.5	32	58	10
38°C	21	50	29	32	52	16
68°C	13	51	36	21	58	21

7 DISCUSSION OF RESULTS

The similarity not only in the structure of the bands of D_2O and H_2O but also in their variations with temperature leads us to the conclusion that the explanation of one of us¹¹ for water applies equally well to heavy water. The objections

by Sutherland¹² to the existence of triple molecules in water were met in another paper.¹³ In a recent communication¹⁴ Cross, Burnham and Leighton, agree with us as to the triplet structure of the water band, but "attach little or no significance to the existence of definite polymolecular structures such as $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ " to which we attribute the two lower frequencies of the water band. They assume in liquid water "a broken down ice structure" having "different coordination types of water molecules," the two coordinated structure predominating in the liquid state. We are unable to understand how their coordinated types of molecules are different from our polymerised or associated types. It is well known that polymerisation is a result of coordination between molecules and we believe that their coordinated types are the same as our associated molecules, though they seem to differentiate between them. Our results with water agree with theirs in indicating a predominance of the double type over the others.

We therefore postulate the existence of single, double and triple molecules even in heavy water, the proportions of which change with temperature. From a comparison of tables IV and V, it is evident that the proportion of triple molecules at any temperature is greater for heavy water than for the lighter one. So the polymerisation appears to be larger in heavy water. This explains generally its higher freezing and boiling points and also its higher temperature of maximum density. There is another conspicuous feature in the variations in the relative proportions of the polymers with temperature. For heavy water the change in the proportions of the three types of molecules from 6° to 30°C and from 65° to 100°C is much larger than from the intermediate range 30° to 65°C. This seems to indicate that the equilibrium between the three polymers is more stable at intermediate temperatures than at temperatures nearer the freezing and boiling points. This explains the minimum specific heat of heavy water approximately in this range as obtained by Brown, Bornes and Mass.¹⁵ Also the higher degree of polymerisation in heavy water than in ordinary water explains its higher specific heat.

REFERENCES

- ¹ *Phys. Rev.*, **46**, 392 (1934).
- ² *Proc. Ind. Acad. Sciences*, **2 A**, 291 (1935).
- ³ *C. R.*, **201**, 667 (1935).
- ⁴ *Journ. Chem. Phys.*, **2**, 461 (1934).
- ⁵ Rao, I.R., *Proc. Roy. Soc., A*, **146**, 480-509 (1934).
- ⁶ Rao, I.R., *loc. cit.*
- ⁷ Rao, I.R., *Proc. Roy. Soc., A*, **130**, 498 (1931).
- ⁸ Rao, I.R. *Proc. Roy. Soc., A*, **146**, 496 (1934).
- ⁹ *Loc. cit.*, p. 500.
- ¹⁰ Rao, I.R., *Proc. Roy. Soc., A*, **146**, 505 (1934).
- ¹¹ *Loc. cit.*
- ¹² Sutherland, *Proc. Roy. Soc., A*, **141**, 535 (1933).
- ¹³ *Loc. cit.*
- ¹⁴ Cross, Burnham, and Leighton, *Jour. Am. Chem. Soc.*, **59**, 1134 (1937).
- ¹⁵ *Can. J. Research.*, **13**, 167 (1933).

THE THEORY OF MOLECULAR DISSOCIATION AND THE FUNDAMENTAL MECHANISMS IN UPPER ATMOSPHERE

By R. C. MAJUMDAR

Bose Research Institute, Calcutta

(Received for publication, March 1, 1938.)

ABSTRACT. In the first article a theoretical formula is developed to estimate the degree of molecular dissociation in upper atmosphere under the action of the ultraviolet light of the sun. In the second article the dissociation of oxygen and nitrogen molecules is discussed and it is found that the oxygen molecules are completely dissociated at a height of about 167 km. i.e., much above E region of the ionosphere, provided we assume a temperature of 300°K. and a molecular weight corresponding to the average mass of nitrogen molecules. In the last article the constituents as well as the mechanism of the fundamental processes in ionosphere are discussed.

INTRODUCTION

Many interesting facts have been revealed in recent years from organised spectroscopic studies¹ of night sky and aurora all over the world regarding the constituents present in the upper atmosphere. Whereas hydrogen and helium are found to be absent and ozone confined only in the lower region between 20 to 50 km., it is remarkable that nitrogen and oxygen, along with some percentage of water vapour have been definitely proved to exist in the upper atmosphere, nitrogen being found to be in molecular state from the occurrence of first negative and Vegard Kaplan bands and oxygen in atomic state from the persistent occurrence of the well known green auroral line ; all attempts, however, to observe atomic nitrogen and molecular oxygen have been proved unsuccessful. These facts together with the results of the investigation carried out in a previous paper MI² are expected to give a complete picture of the state of affairs in ionosphere. We have found in MI that the theoretical formula for the collision frequency per electron calculated for the interaction between electrons and positive ions agrees satisfactorily well with that obtained from the observation on the reflection coefficient of the radio waves provided we assume that in F layer the number of electrons per cm.³ as revealed by the radio measurement is very nearly equal to the number of ions per cm.³ and in E layer the latter outnumbering the former by a

factor of the order of 100; an immediate conclusion follows, therefore, that the electrons and ions are the chief agents in causing the dispersion and absorption of radio waves in E and F layers, the dispersion being affected directly by the vibration of the electrons whereas the absorption by their encounter with the positive ions.* This high ionic density in E layer of the order of 10^7 is also required for the reconciliation of the estimated electrical conductivity as deduced from wireless observations with the estimates made from the data of terrestrial magnetism.³ [Appleton's original estimation was $n^+ \sim 10^8$ to 10^9 per c.c.]

We have therefore got the following two fundamental problems to solve: Firstly, whether the experimental results of night sky and auroral spectra are to be interpreted as it may seem obvious that oxygen exists in upper atmosphere only in the atomic state, *i.e.*, completely dissociated by sunlight and nitrogen instead of being dissociated get ionised, possibly as a result of fluorescent radiation emitted by the atoms in sun's atmosphere, or oxygen does exist in the molecular state as well, the stronger bands of which being in the ultraviolet regions not being detected so far due to atmospheric absorption and nitrogen may also exist in the atomic state. The problem at present can be answered only by theoretical investigation and will evidently throw much light as to the constituents present in the upper atmosphere. And secondly, how to account for the difference, mentioned, in the number of electrons with respect to positive ions in these ionospheric layers, *i.e.*, in F layer they are equal, whereas in E layer the electrons are in deficiency by a factor 100 over the positive ions. The pursuit of this question together with the knowledge of the laboratory experiments on the collision cross-sections for recombination of electrons and positive ions and for attachment and detachment of electrons to and from the neutral particles shall enable us to understand the fundamental mechanism in ionosphere.

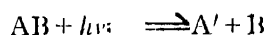
The present paper makes a preliminary theoretical investigation of the above questions. In the first article a general formula is derived for the estimation of the degree of molecular dissociation at different heights in upper atmosphere under the action of the ultraviolet light of the sun. In the second article the formula is applied to find out the degree of dissociation of oxygen and nitrogen molecules, and in conclusion, discussions are given in the light of the above results on the mechanisms of the fundamental processes in ionosphere.

§1. *The equation of molecular dissociation in a non-isothermal system.* Let us consider a system of molecules at an equilibrium temperature T dissociating into their constituent atoms under the action of radiation from a source emitting like a black body at a temperature T_0 which is different from the temperature T of the gas molecules. We shall accordingly obtain a continuous spectrum in absorption starting from a wave length corresponding to the dissociation

* The contribution to the collision frequency as the result of electrons encountering with the neutral particles will be discussed in a subsequent paper.

energy of the molecule and extending to the shorter wave length side, corresponding to the increase of the kinetic energy of the atoms after dissociation. From a study of the absorption and emission coefficients in the continuous spectrum it will be possible to find out an expression for the degree of dissociation of molecules in such a system, which is not in a temperature equilibrium.

The mathematical theory of continuous absorption in case of atoms dissociating into ions and electrons under the action of light has been studied by Milne⁴ by introducing probability coefficients for the mechanism of ionisation by incident radiation and of recombination of electrons with the ions. With the assumption that in the state of thermodynamical equilibrium the number of different types of particles taking part in the reaction must satisfy Saha's equation, Milne obtained a relation between these probability coefficients; the rigorous evaluation of these coefficients separately was, however, carried out by Krammers, Oppenheimer, Gaunt, Sommerfeld and others.⁵ Following Milne, Pannekoek⁶ developed a theory for the dissociation process taking place in a non-isothermal system and obtained a modified Saha's equation, which he applied successfully to explain the observed concentration of free electrons in upper atmosphere at a temperature T caused by the ionisation of molecules into molecular ion and electron under the action of the ultraviolet radiation of the sun, emitting like a black body at a temperature say T_0 , which is different from the temperature T of the ionosphere. We shall also adopt a similar method as that of Milne and Pannekoek in investigating the present problem of dissociation of molecules into their constituent atoms under the influence of external radiation. Let us assume thereby that under the action of light of frequency ν , the molecule AB is dissociated into a normal and an excited atom given respectively by B and A'. Symbolically written it runs as follows:



Let ν_0 be the frequency at which the continuous absorption bands just appear. The energy $h\nu_0$ is thus required for the dissociation of molecule AB into atoms A and B and at the same time for the excitation of the atom A to A', i.e.,

$$h\nu_0 = D + I \quad \dots (1)$$

where D is the heat of dissociation and I that of excitation

Under the action of radiation of frequency $\nu > \nu_0$ the molecule AB is dissociated and a continuous absorption band is formed from ν_0 extending to $\nu = \infty$, the dissociated atoms flying off with the relative kinetic energy

$$\frac{1}{2} MV^2 = h\nu - h\nu_0 \quad \dots (2)$$

where M is the reduced mass given by

$$M = \frac{m_A m_B}{m_A + m_B} \quad (3)$$

and V is the component of the relative velocity in the direction of the lines joining the centres of the atoms.

Let n_{AB} , n_A , and n_B be the equilibrium concentrations of molecules AB , free atoms A and B respectively. The number of absorption processes per second under the action of monochromatic radiation of density ρ_ν from the continuous spectrum is given by

$$n_{AB} \psi_\nu c \rho_\nu dv / h\nu \quad \dots (4)$$

The probability coefficient for absorption ψ_ν has values only for $\nu > \nu_0$.

Whereas the corresponding number of recombination processes is

$$4\pi n_A n_B \beta_\nu \left(1 + \frac{c^3}{8\pi h\nu^3} \rho_\nu\right) \left(\frac{M}{2\pi kT}\right)^{\frac{3}{2}} e^{-MV^2/2kT} V^3 dV \quad \dots (5)$$

where β_ν denotes the probability coefficient for recombination process in the continuous emission band.

By equating the two processes and with the help of (2) we obtain at once the condition of equilibrium as follows:

$$\frac{n_{AB} \psi_\nu c \rho_\nu dv}{h\nu} = 4\pi n_A n_B \beta_\nu \left(1 + \frac{c^3}{8\pi h\nu^3} \rho_\nu\right) \left(\frac{M}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{MV^2}{2kT}} V^2 \frac{h}{m} dv \quad \dots (6)$$

In the case of isotropic radiation of temperature T when ρ_ν is given by the Planck's formula we have the dissociation formula, usually called the reaction isochore, as follows:

$$\frac{n_A n_B}{n_{AB}} = K_0 \quad \dots (7)$$

where K_0 is the equilibrium constant for the dissociation of the molecule AB in atoms A and B and is given by⁷

$$K_0 = G \frac{s}{hr_0} \left(\frac{MkT}{8\pi}\right)^{\frac{1}{2}} e^{-D/kT} \left(1 - e^{-h\omega/kT}\right) \quad \dots (8)$$

$$\text{where } G = \frac{G_A G_B}{G_{AB}} \quad \dots (9)$$

ω = fundamental vibrational frequency of the molecule,

G_A, G_B = statistical weights of the normal quantum state of the free atoms,

G_{AB} = statistical weight of the ground state of the electronic configuration of the molecule, the nuclei being regarded as fixed,

r_0 = equilibrium distance between the atoms,

s = symmetry number of a molecule. It is equal to *unity* if two atoms A and B are intrinsically different whereas it is *two* if the two atoms are identical.

Further we have from Boltzmann's law

$$\frac{n_{A'}}{n_A} = \frac{G_{A'}}{G_A} e^{-E/kT} \quad \dots \quad (10)$$

Thus we obtain

$$\frac{\psi_v c \rho_v}{h\nu} = \frac{G'_s}{2\pi r_0^2} \frac{MV^2}{kT} e^{-h\nu/kT} \beta_v \left(1 + \frac{c^3}{8\pi h\nu^3} \rho_v\right) \left(1 - e^{-h\nu/kT}\right) \quad \dots \quad (11)$$

where

$$G' = \frac{G_A \cdot G_B}{G_{AB}} \quad \dots \quad (12)$$

Now since

$$\rho_v = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} ; 1 + \frac{c^3}{8\pi h\nu^3} \rho_v = \frac{e^{h\nu/kT}}{e^{h\nu/kT} - 1} \quad \dots \quad (13)$$

we obtain the relation between the coefficients

$$\beta_v = \frac{8\pi^2 r_0^2}{c^2 G_s} \frac{kT}{\frac{1}{2} MV^2} \nu^2 \left(1 - e^{-h\nu/kT}\right) \quad \dots \quad (14)$$

When conditions do not correspond to thermal equilibrium the equation (6) must be multiplied by $h\nu$ and integrated over all frequencies, thus ensuring the conservation of energy during the process. We therefore obtain, when the relation (14) is substituted in it,

$$\frac{n_A n_B}{n_{AB}} = K_0 \frac{c^3}{8\pi h} \int_{\nu_0}^{\infty} \frac{\psi_v \rho_v d\nu}{\psi_v \nu^2 \left(1 + \frac{c^3}{8\pi h\nu^3} \rho_v\right) e^{-h\nu/kT} d\nu} \quad \dots \quad (15)$$

For the evaluation of the integrals on the right hand side a knowledge of the absorption coefficient ψ_ν in the continuous region as a function of the

frequency ν is required, which is however very complicated in general for molecules. But in case the absorption coefficient shows a sharp maximum for any particular wave-length falling off rather rapidly on both sides of it, the evaluation of (15) may be easily carried out without much appreciable error by replacing ψ_ν by its maximum value ψ_m and assuming it constant within the short range of integration where only it has positive values. Further, assuming that the velocity distribution of the electrons are given by Maxwell's distribution law at a temperature T , which is different from the temperature T_0 of the black body radiation emitted by the sun and neglecting the effect of the stimulated emission we obtain under the above circumstances,

$$\frac{n_A n_B}{n_{AB}} = K_0 \frac{T_0}{T} e^{-\frac{h\nu_0}{k} \left(\frac{T}{T_0} - 1 \right)} = K_1 \quad \dots (16)$$

$$\text{where } K_1 = \frac{G's}{h\nu_0^2} \left(\frac{M}{8\pi} \right)^{\frac{1}{2}} \frac{k^{\frac{3}{2}} T^{\frac{1}{2}}}{kT} T_0 e^{h\nu_0/kT} e^{-h\nu_0/kT_0} \left(1 - e^{-h\nu/kT} \right) \quad \dots (17)$$

$$\text{or } \frac{n_A' n_B}{n_{AB}} = \frac{G's}{G_A} K_0 \frac{T_0}{T} e^{-\left(\frac{h\nu_0}{kT_0} - \frac{D}{kT} \right)} = K_2 \quad \dots (18)$$

$$\text{where } K_2 = \frac{G's}{h\nu_0^2} \left(\frac{M}{8\pi} \right)^{\frac{1}{2}} \frac{k^{\frac{3}{2}} T^{\frac{1}{2}}}{kT} T_0 e^{-h\nu_0/kT_0} \left(1 - e^{-h\nu/kT} \right) \quad \dots (19)$$

If now x is the degree of dissociation, *i.e.*, the fraction of the molecules that are dissociated and P the total pressure of the gas mixture expressed in atmospheres, we can write down the above equation as follows :

$$\frac{x^2}{1-x^2} P = K \quad \dots (20)$$

$$\text{where } K = \frac{1}{10^6} \frac{G's}{h\nu_0^2} \left(\frac{M}{8\pi} \right)^{\frac{1}{2}} \frac{k^{\frac{3}{2}} T^{\frac{1}{2}}}{kT} T_0 e^{-x/kT_0} \left(1 - e^{-h\nu/kT} \right) \quad \dots (21)$$

χ = the energy required for dissociation as well as for excitation.

To obtain the degrees of dissociation in the actual ionosphere at a particular height the right hand side of the equation (20) must be multiplied by a factor $e^{-\psi_{\max} N' H P}$, where $\psi_{\max}$ is the maximum value of the molecular absorption

coefficient, N' the number of molecules per cm^3 for one atmosphere and H the equivalent height of one atmosphere, and by a factor β the so called dilution factor; the first factor representing the weakening of the active solar radiation due to its absorption caused by the dissociation of the molecules above the layer under consideration and the second one giving the field due to the dilute temperature radiation. β is given by ⁸

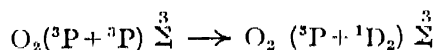
$$\beta = \frac{R^2}{4r^2} \quad \dots (22)$$

where R is the radius of the sun and r the distance from the sun of the point at which the dissociation is calculated.

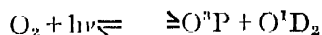
We thus obtain finally the formula for molecular dissociation in upper atmosphere as follows :

$$\frac{x^2}{1-x^2} P = \beta K e^{-\psi_{\max} N' H P} \quad \dots (23)$$

§ 2. (a) *Dissociation of Oxygen Molecules in upper Atmosphere.* Before we apply the formula (23) to the case of oxygen molecules and calculate the degree of dissociation at different heights, let us first summarise the experimental evidences ⁹ on the band spectrum of oxygen molecule in the region of continuous absorption in which we are particularly interested in the present paper. The most important bands of O_2 molecule are the Runge-Schuman bands, which starting $\lambda 2000\text{\AA}$ pass to the continuous absorption at $\lambda 1750\text{\AA}$. According to Mulliken it corresponds to the transition



The continuous absorption at $\lambda 1750\text{\AA}$, as pointed out by Herzberg, is due to the photochemical dissociation of O_2 -molecules into a normal ^3P and an excited ^1D atom according to the process.



the energy required for this being

$$\chi = 7.05\text{V} = \text{D} + \text{E}$$

where $\text{D} = 5.09\text{V}$ is the heat of dissociation of O_2 -molecules into two normal O^3P atoms and $\text{E} = 1.96\text{V}$, the heat of excitation of O^3P atom to the O^1D_2 state. The

absorption continues up to λ 1250 Å and the portion of it beyond λ 1750 Å corresponds to the increase of the kinetic energy of the constituent atoms after the dissociation process. We shall be chiefly interested in the continuous absorption taking place between λ 1750 Å and λ 1250 Å as a result of the dissociation of the molecules under the action of the ultraviolet radiation from the sun having wave length $\lambda < 3000$ Å. The spectrum in this region has been thoroughly investigated by Ladenburg and Van Voorhis.¹⁰ They find a sharp maxima in the absorption at λ 1450 Å and such that a length of 0.0014 cm. of O₂ at N. T. P. reduced the light of this wave-length to about half of its intensity, *i.e.*, as much as metallic absorption. We have therefore for O₂-molecule assuming $T=300^\circ\text{K}$ (ionosphere) and $T_0=6000^\circ\text{K}$ (sun), $\log \beta K=5.48$, $\log \psi_\nu$ (max) = 17.26; $\log H=5.96$ (corresponding to average mass of nitrogen molecules)¹⁴ and $\log N'=19.39$. It follows therefore

$$\frac{x^2}{1-x^2} = \frac{3 \cdot 10^{-5}}{P} e^{-4 \cdot 1 \cdot 10^8 P} \quad \dots (24)$$

We tabulate the numerical results in the following :—

P = pressure in Atmosphere, h = height in kilometer, x = degree of dissociation.

10^{-7}	146	10^{-8}
10^{-8}	167	.991
10^{-9}	188	1
10^{-10}	209	1

We find therefore that above 167 km., *i.e.*, much above E layer and at a temperature of 300°K the oxygen molecules are completely dissociated into its constituent atoms. The maximum dissociation occurs at a layer where the total number of molecules per cc. are given by

$$(N'P)_{\max} = \frac{1}{\psi_{\max} H} \sim 6 \cdot 10^{10} \quad \dots (25)$$

(b) *Dissociation of Nitrogen molecules.*⁹ It is found from laboratory experiments that nitrogen is relatively transparent up to λ 1450 Å, where it possesses narrow discrete bands which absorb radiation between 1450–1000 Å. The absorption is complete when the light has traversed a layer equivalent to 40 cm. of the gas at N. T. P. The sharp N₂ bands shows that the molecule is not dissociated by absorption of light λ 1450 Å, which corresponds to the dissociation energy of N₂ but it is simply excited to higher stable states. An examination of the potential curves of nitrogen molecules for normal and excited states also shows that it is quite unlikely that the molecule will be dissociated. A continuous region of spectrum, however,

Theory of Molecular Dissociation, etc.

appears at about λ 661 Å corresponding to the second ionisation potential 18 which therefore indicates the photo-ionisation of the nitrogen molecule. We therefore assume that the upper atmosphere above the E region will consist n of oxygen in atomic states and nitrogen in molecular state.

§3 *Discussion.* The present paper, as mentioned in the introduction, only a preliminary attempt to estimate the degree of molecular dissociation at different heights in ionosphere, with a view to discuss its constituents and the fundamental mechanism of the process taking place there. We should to point out that our conclusion will be only qualitative, since we have substituted in our numerical calculations the maximum value of the absorption coefficient λ 1450 Å and assumed it constant throughout the range of integration ; a rigorous quantitative investigation should, however, take account of the proper value of the absorption coefficient obtained theoretically ¹¹ as a function of frequency. The results given in the table however, shows that the oxygen molecules remain practically undissociated at a height of 146 km. and then the dissociation suddenly almost completed at a height of 167 km. This is due to the simplified assumptions we have just mentioned. Considering the variation of the absorption coefficient with wave-length we can easily find that the dissociation will spread over a height of the order of 30 km., i.e., dissociation at each level will take place earlier by this amount of height and it will therefore be quite probable that the oxygen molecules are dissociated at least quite appreciably even up to a height of 130 km. Further the number of oxygen atoms as given by (10) agrees fairly well with the tentative estimation of Chapman and is sufficient for the production of the requisite number of metastable atoms which are required to explain the intensity of the green light (λ 5577 Å) of the night sky spectrum as observed particularly by McLennan and Rayleigh. The layer of atomic oxygen lying at a height above the E region is thus a possible source of the greenlight. These results, that is, the upper atmosphere above a height of E layer consists mainly of atomic oxygen and molecular nitrogen (also some percentage of water vapour), when incorporated in the investigations of an earlier MI, as mentioned in the introduction enable us to analyse the fundamental mechanisms as regards the various processes taking place in ionosphere. For the purpose we collect first the relevant data regarding these layers :

Layer	height in km.	n in cc.	n^+ in cc.	N in cc.	V in cm/per sec.	Δ per sec.	T in degree Abs.
F layer	~300	10^6	10^6	10^6	$1.7 \cdot 10^7$	10^3	10^3
E layer	~100	10^7	10^7	10^{14}	$9.5 \cdot 10^6$	$2 \cdot 10^5$	$3 \cdot 10^2$

Fundamental process.	cross section in cm^2 .	velocity variation.	pressure variation.
$\text{N}_2^+ + e \rightarrow \text{N}_2$ (recombination) ...	$5 \cdot 10^{-17}$	$1/v^2$	none
$\text{O} + e \rightarrow \text{O}^- + h\nu$ (attachment) ...	$1.3 \cdot 10^{-16}$	$1/v^2$	none
$\text{O} + \text{O} \rightarrow \text{O}_2 + e$ (detachment) ...	.		

The data for n and n' are taken from the paper MI, and N , the total number of particles per cm^3 calculated after Maris and Hulbert¹², assuming that the mean molecular mass of the atmosphere is equal to that of molecular nitrogen. The cross-sections for the fundamental processes, calculated for a temperature of 300°K , are reproduced from a paper by Bradbury.¹³

Now what are the reasons that in E layer the number of ions per cm^3 outnumber the electronic concentration by a factor of the order of 100 and in F layer they are equal and that the collision frequency per electron as measured from the reflection coefficient of radio waves correspond to the collision of the electrons with the positive ions only? The answer to this question will give us an understanding of the processes in these layers. It can, however, be better understood with reference to the consideration of the magnitude of probabilities of these different processes. Since the rate of loss of electron density due to recombination and attachment processes at night are given respectively by¹³

$$\frac{dn}{dt} = -v Q^r(v) n' n \quad \text{and} \quad \frac{dn}{dt} = -v Q^a(v) N n$$

where v is velocity of the electron and $Q(v)$ the effective cross-section for electrons of velocity v , we obtain the ratio of the loss of the particles due to these processes as given by

$$\frac{\text{Loss due to recombination}}{\text{Loss due to attachment}} = \frac{n'}{N} \frac{Q^r(v)}{Q^a(v)}$$

$$\sim 10^{-4} \quad \text{for E layer}$$

$$\sim 4 \cdot 10^2 \quad \text{for F layer}$$

The rate of recombination per electron in E and F layers are $4.7 \cdot 10^{-8}$ and $2.3 \cdot 10^{-4}$ respectively, the coefficients of recombination $\alpha = Q(p) \cdot v$ being

$4.7.10^{-10}$ and $2.5.10^{-10}$.* This slow rate of recombination, which is also required from the observations, together with the fact that the observed collision frequency per electron is due mainly to its encounter with the positive ions only, the neutral particles being practically out of the scene, strongly suggests that the disappearance of electrons in both E and F layers during the night is caused chiefly by the recombination of electrons with positive ions. An examination of the rate of loss of electrons by recombinations and that by attachment offers then an easy explanation for the ratio of the number of electrons to that of the ions in E and F layers as mentioned above. The preponderance of attachment process over the recombination and the deficiency of electrons over the ions by a factor 100 in E layer show that the number of electrons initially produced by the ionisation of molecules shall set up a sort of local equilibrium with the negative ions as a result of rapid attachment and detachment processes[†] to and from the neutral particles until their ratio has reached the stationary value 300,† while the loss of electrons, however, being ultimately governed by their recombination with the ions. In F layer on the other hand the recombination is more rapid than the attachment and therefore the numbers of electrons initially produced shall also be equal to the numbers of positive ions, there being practically no attachment to the neutral particles.

The quantitative investigation of the problem of dissociation as well as of the fundamental processes in ionosphere is reserved for subsequent communication.

I am grateful to Professor M. N. Saha for kindly drawing my attention to this interesting problem of ionosphere and to Professor D. M. Bose for his interest and encouragement.

* The effective coefficients of recombination for E and F layers as defined by³

$\alpha' = \alpha \left(1 + \frac{n^-}{n^+} \right)$, n^- being the negative ion density, are $1.4.10^{-7}$ and $2.5.10^{-10}$ respectively.

† Massey has also recently drawn attention to this problem from the consideration of the magnitudes of various collision processes in ionosphere. The present paper, though it was nearly ready for publication, has undergone a little alteration after Massey's paper. It follows from his result that the attachment should also be equally important in F layer and there would be nearly the same equilibrium ratio between the electrons and ions as in E layer as a result of attachment and detachment processes. But as the concentration of electrons in F layer is equal to that of ions, Massey passes over the difficulty by concluding that the gas or gases present there have very little electron affinity and they are therefore nitrogen. This conclusion, however, cannot be reconciled with the observed facts that in ordinary aurora the green line of atomic oxygen (λ 5577Å) and in sunlit aurora the red oxygen line λ 6300 Å is prominently strong, showing therefore the great abundance of oxygen atoms even up to a height of 1000 km. For a quantitative elucidation of this important point we should investigate the whole problem from a consideration of the statistical equilibrium between all the elementary fundamental processes in ionosphere.

REFERENCES

- ¹ G. DeJardin, *Rev. Mod. Phys.*, **8**, 1 (1936).
E. W. Hewson, *Ibid*, **9**, 403 (1937).
- ² R. C. Majumdar, *Zs. f. Phys.*, **107**, 599 (1937); This paper shall be referred as MI.
- ³ S. Chapman, *Proc. Roy. Soc., A.*, **132**, 353 (1931); *Ibid*, **141**, 705 (1933).
E. A. V. Appleton, *Proc. Roy. Soc., A.*, **162**, 451 (1937).
- ⁴ E. A. Milne, *Phil. Mag.*, **47**, 209 (1924).
- ⁵ H. A. Kramers, *Phil. Mag.*, **46**, 836 (1923).
J. R. Oppenheimer, *Zs. f. Phys.*, **56**, 725 (1929).
J. A. Gaunt, *Phil. Trans., A.*, **229**, 163 (1930).
A. Sommerfeld, *Ann. d. Phys.*, **11**, 257 (1931).
- ⁶ A. Pannekoek, *Proc. Roy. Acad. Amsterdam*, **29**, 1165 (1926).
S. Chapman, *Proc. Roy. Soc.*, *loc. cit.*
- ⁷ G. E. Gibson and W. Heitler, *Zs. f. Phys.*, **49**, 465 (1928).
S. Rosseland, *Theoretical Astrophysics*, 1936, p. 245.
R. H. Fowler, *Statistical Mechanics*, 1936, 2nd ed., Chap. V.
- ⁸ S. Rosseland, *Loc. cit.*, p. 145 and p. 319.
- ⁹ M. N. Saha, *Proc. Nat. Inst. of Sciences in India*, **1**, 217 (1935); *Proc. Roy. Soc., A*, **160**, 155 (1937).
S. Chapman and W. C. Price, *Reports on Progress in Physics*, **11**, 42 (1937).
- ¹⁰ R. Ladenburg and C. C. Van Voorhis, *Phys. Rev.*, **43**, 315 (1933).
- ¹¹ E. C. G. Stueckelberg, *Phys. Rev.*, **42**, 518 (1932).
- ¹² E. O. Hulbert, *Rev. Mod. Phys.*, **9**, 44 (1937).
- ¹³ N. H. Bradbury, *Journal of Applied Phys.*, **8**, 709 (1937).
- ¹⁴ D. F. Martyn and O. O. Pulley, *Proc. Roy. Soc., A.*, **164**, 455 (1936).
H. S. W. Massey, *Proc. Roy. Soc., A.*, **163**, 542 (1937).

STRUCTURE OF AROMATIC COMPOUNDS, PART III BENZOPHENONE

By K. BANERJEE, D. Sc.,
Reader in Physics, Dacca University

AND

A. HAQUE, M.Sc.,
Imperial College of Science and Technology, London

(Received for publication, March 10, 1958.)

ABSTRACT. Cell dimensions of benzophenone have been determined by rotation photographs to be $a_0 = 10.17 \text{ \AA}$, $b_0 = 12.06 \text{ \AA}$, and $c_0 = 7.98 \text{ \AA}$, with 4 molecules per unit cell. From a combination of oscillation and Weissenberg camera photographs the space-group has been found to be $D_2^2P_{21}2_12_1$. From considerations of the magnetic anisotropy of the crystal the two benzene rings in the benzophenone molecule has been found to be inclined to each other at 135° nearly, the connecting C atom lying at the intersection of these two planes. The line bisecting the acute angle between these planes lies along the b -axis, while the mean plane is inclined to the c -axis by $22^\circ 25'$.

In part II of the present series¹ of communications, the structure of benzil was determined, the problem being much simplified due to its similarity to that of dibenzil. In that case the valency bonds binding the carbon atoms are identical. Such similarity, however, cannot be assumed *a priori* in cases where two benzene rings are linked together by atoms other than aliphatic carbon. Benzophenone is such a substance whose structure might throw some light on a different type of linking of the benzene rings. A determination of the structure of this compound will be discussed in this paper.

In the case of benzophenone, the coupling of two benzene rings is through one CO group and for this reason this substance has been taken for analysis in the present investigation.

Benzophenone (Groth's *Chemische Krist*, Vol. V, page 102) belongs to the orthorhombic bispinoidal class with the following axial ratio:—

$$a : b : c = 0.8511 : 1 : 0.6644.$$

The substance was crystallised from a mixture of water and alcohol; long needle shaped crystals were obtained.

From the measurements of the rotation photographs, the axial lengths are found to be

$$a_0 = 10.30, \quad b_0 = 12.11, \quad c_0 = 8.04$$

in Angstrom units.

The sp. gravity of the crystal was determined by balancing fine particles of crystals from a solution of zinc sulphate in water. It is found to be 1.198, which is slightly higher than the value given in International Critical Table, Vol. I, page 248.

Since the molecular weight is 182, the number of molecules per unit cell is 4.

Nine oscillation photographs of 10° range about the c -axis of the substance were taken. A Weissenberg photograph of the central layer line for rotation about the b -axis was taken. The reflecting planes were identified and the results of the measurements are given in the following table. The asterisks indicate that the corresponding planes were obtained on the Weissenberg photograph as well and hence the estimates of intensity are much more reliable than with the other planes.

TABLE

List of Reflecting planes of Benzophenone

Axial planes.

Planes.	Intensity.	Planes.	Intensity.
040	V.W.	002	V.S.*
080	W.	200	V.S.
0(10)0	M.W.	400	M.S.
0(12)0	W.		

Prism planes.

Planes.	Intensity.	Planes.	Intensity.
033	S.	061	M.W.
044	V.V.W.	062	M.W.
051	V.W.	063	M.W.
053	V.W.	073	V.W.

Prism planes (continued).

Planes.	Intensity.	Planes.	Intensity.
0(10)1	V.W.	2(10)0	V.V.W.
0(10)2	V.W.	2(11)0	W.
101	V.S.*	2(12)0	W.
102	V.S.*	330	S.
103	M.S.*	350	W.
202	V.S.*	360	V.W.
203	M.W.*	370	M.W.
204	M.W.*	380	W.
302	V.S.*	3(11)0	V.W.
303	M.W.*	410	V.S.
304	M.W.*	420	S.
402	M.W.*	430	W.
403	S.	450	W.
501	W.*	510	W.
503	M.S.	530	V.W.
120	V.S.	540	W.
130	V.S.	550	S.
140	V.S.	560	W.
160	V.W.	570	M.S.
190	M.S.	580	V.W.
1(10)0	M.W.	590	W.
1(11)0	M.W.	5(10)0	W. ¹
1(13)0	V.W.	610	S.
210	W.	620	M.W.
220	V.S.	630	V.W.
230	M.W.	640	V.W. ¹⁰²
250	V.S.	650	V.W.
260	V.S.	660	W.
270	M.S.	670	W.
280	V.V.W.	710	W.

Prism planes (continued).

Planes.	Intensity.	Planes.	Intensity.
720	M.W.	860	V.W.
730	V.W.	870	V.W.
740	M.W.	920	V.W.
780	W.	930	V.V.W.
820	M.W.	960	V.W.
830	V.V.W.	(10)20	V.W.
840	V.W.	(10)60	V.W.

General Planes.

Planes	Intensity	Planes	Intensity
121	V. S.	193	V. V. W.
122	V. S.	1 (10) 1	V. W.
123	V. S.	1 (10) 3	W.
132	S.	1 (11) 1	W.
133	V. S.	1 (11) 2	M. W.
134	M. W.	1 (12) 1	W.
141	M. S.	1 (12) 2	M. S.
142	M. W.	1 (13) 2	V. V. W.
143	S.	1 (13) 3	V. V. W.
144	W.	1 (14) 1	V. V. W.
152	V. W.	211	V. S.
153	M. W.	212	V. S.
161	M. S.	213	S.
162	W.	221	M. S.
163	W.	222	V. S.
173	W.	223	V. S.
181	M. S.	231	M. S.
182	V. W.	232	V. S.

General Planes (continued).

Planes.	Intensity.	Planes.	Intensity.
241	V. S.	322	M. S.
243	W.	323	S.
251	M. S.	331	V. S.
252	M. S.	333	V. S.
253	V. W.	331	M. W.
262	S.	332	V. S.
263	S.	334	M. W.
272	M. W.	351	M. S.
273	M. W.	352	M. W.
281	V. W.	353	W
282	W.	354	V. W.
283	V. V. W.	361	M. W.
293	M. W.	362	M. S.
294	M. W.	363	V. W.
2(10)1	W.	371	M. W.
2(10)2	M. W.	372	M. W.
2(10)3	W.	373	V. V. W.
2(11)1	V. W.	381	V. W.
2(11)2	V. V. W.	382	V. V. W.
2(11)3	V. W.	383	M. W.
2(12)1	V. V. W.	392	V. W.
2(12)2	V. V. W.	3(10)1	V. V. W.
2(12)3	V. W.	3(10)2	V. W.
2(13)2	V. V. W.	3(11)1	V. W.
2(13)3	V. W.	3(11)3	V. V. W.
311	M. W.	3(12)3	V. V. W.
312	S.	411	V. S.
313	S.	412	W.
314	V. V. W.	413	M. W.
321	V. S.	414	W.

General Planes (continued).

Planes.	Intensity.	Planes.	Intensity.
421	V. S.	563	M. W.
422	V. S.	573	V. W.
423	M. W.	582	M. W.
431	V. S.	591	V. W.
432	V. S.	592	W.
433	V. W.	5(10)2	W.
451	V. W.	611	M. W.
452	M. W.	612	M. W.
454	W.	613	M. W.
461	V. W.	621	M. W.
472	V.V. W.	622	W.
473	M. W.	633	M. W.
481	M. S.	641	V. V. W.
482	V. W.	642	V. W.
483	M. W.	652	V. V. W.
491	M. W.	662	W.
493	W.	663	M. W.
4(10)3	W.	672	V. W.
511	S.	673	V. W.
512	V. S.	681	W.
513	W.	683	V. W.
521	S.	691	W.
522	W.	712	M. W.
523	W.	713	M. W.
531	V. S.	721	M. W.
542	W.	732	M. W.
543	M. W.	733	W.
544	V.V.W.	751	V.V.W.
551	M. W.	753	V.W.
562	V. W.	761	M.W.

General planes (continued).

Planes.	Intensity.	Planes.	Intensity.
762	W.	931	W.
771	V. W.	941	V.V.W.
772	W.	942	W.
773	V.V.W.	951	V.V.W.
782	W.	953	W.
783	V.V.W.	961	V.V.W.
821	M.W.	971	V.V.W.
822	M.W.	972	V.V.W.
831	V.V.W.	981	V.V.W.
832	M.W.	982	V.V.W.
841	M.W.	991	V.V.W.
851	M.W.	9(11)3	W.
871	M.W.	(10)61	V.V.W.
911	V.V.W.	(10)81	V.V.W.

From an examination of the list of the reflecting planes, it is observed that *hoo*, *oko* and *ool* planes are absent when *h*, *k* and *l* respectively are odd. There is no other systematic absence of planes. Hence there are three two-fold screw axes along the three crystallographic axes. Hence the space-group is $D_2^1 P 2_1 2_1 2_1$.

The magnetic susceptibilities of this crystal were measured by Krishnan, Banerjee and Guha,² along the three axes and the following values were obtained

$$\chi_a = -88.0 \times 10^{-6}$$

$$\chi_b = -88.6 \times 10^{-6}$$

$$\chi_c = -149.3 \times 10^{-6}$$

The molecule of benzophenone contains two benzene rings joined by a CO group. This carbon atom being an aliphatic one, its contribution towards the magnetic anisotropy may be neglected. We may consider the susceptibilities of the benzene rings of this molecule to be the same as those in diphenyl for which Krishnan, Banerjee and Guha find that the susceptibilities along molecular axes are given by $K_1 = K_2 = 66.9 \times 10^{-6}$ and $K_3 = 174.7 \times 10^{-6}$. Since χ_a and χ_b are nearly equal and are both greater than K_1 and K_2 , a natural assumption is that the two rings are inclined to each other, and the line of intersection of the two

benzene planes are inclined to the "a" and "b" axes. From the dimension of the cell it is easily seen that this axis is the b-axis, for the b-axis is nearly double the usual lateral dimensions of the benzene ring while the a-axis is very nearly the length of diphenyl molecule. The plane bisecting the acute angle between the two benzene planes is normal to the c-axis which corresponds to the maximum diamagnetic susceptibility. The inclination between the two benzene rings may be easily calculated as follows:

We have

$$\chi_a + \chi_b + \chi_c = -325.9 \times 10^{-6}$$

$$K_1 + K_2 + K_3 = -308.5 \times 10^{-6}$$

Hence the total contribution of the CO group is

$$= -17.4 \times 10^{-6}$$

and the contribution along each of the axes

$$= -5.8 \times 10^{-6}$$

$$\text{Hence } K'_1 = K_1 + 5.8 \times 10^{-6} = 72.7 \times 10^{-6}$$

$$K'_2 = K'_1 \text{ and } K'_3 = 180.5 \times 10^{-6}$$

But if 2θ be the acute angle between the two benzene rings, then

$$\chi_a = K'_1 \cos^2 \theta + K'_3 \sin^2 \theta$$

or

$$\sin^2 \theta = \frac{\chi_a - K'_1}{K'_3 - K'_1}$$

Whence $\theta = 22^\circ 35'$ nearly. So the obtuse angle between the two rings is $134^\circ 50'$.

Since $\chi_a = \chi_b$ the molecule is inclined to the b-axis through this same angle of $22^\circ 35'$.

REFERENCES

1. K. Banerjee and K. L. Sinha, *Ind. J. Phys.*, **11**, 21 (1937).
2. K. S. Krishnan, B. C. Guha and S. Banerjee, *Phil. Trans.*, **233**, 235 (1933).

CATHODIC SPUTTERING

By U. K. BOSE, M.Sc.,

Physics Department, Lucknow University, Lucknow, India

(Received for publication, February 24, 1938.)

ABSTRACT. Variation of sputtering with pressure has been investigated quantitatively. It is found that there is a pressure for which the sputtering is maximum; below this pressure the sputtering decreases very rapidly, and above it the sputtering changes hyperbolically.

Zone formation of the usual type has been investigated. Observations show that the sputtered particles form a pseudo-gas.

Some data pertaining to approximate pressure, current, length of dark space, and time of exposure for obtaining films of Cu, Ag, Ni, Fe and Al are given.

Cathodic sputtering was first noticed by Grove in 1852. Since then papers on the subject have appeared spasmodically. The summary of the work done and bibliography up to 1926 has been given by Guntherschultze¹ and Blechschmidt.² Langmuir and T. C. Compton in their article on "Discharge of Electricity through Gases" in Review of Modern Physics, 1930, p. 186, sum up the state of things up to 1930, with special reference to the impact theory of cathodic sputtering.

The great complications of a self sustained discharge with its glows and dark spaces make the quantitative determination of the conditions in a sputtering experiment very difficult. We may note as an exception the work of the research staff of G.I.C. who tried to eliminate these complications but their investigations were confined to very few substances; so is the case with the extension by Langmuir and Kingdom.

Further, as has been recently shown by Jhonson and Harris,³ there are some other secondary effects simultaneously existing in a sputtering experiment in a self sustained discharge. They maintain that there are appreciable number of fast neutral atoms moving perpendicular to the electrodes which are capable of resputtering a deposited layer. Electrons having energy more than 2,000 volts show similar effect.

The various parameters involved in the phenomenon, as has been shown in previous work, are apart from the gas and the cathodic metal (1) the geometry of the apparatus, (2) the temperature of the cathode, (3) the current through the tube, (4) the voltage applied to the tube and consequently the dark space, (5) the pressure of the residual gas, and (6) the time of sputtering. All the quantita-

tive experiments so far carried out were directed to find relations between the amount of sputtering and each of the above mentioned parameters.

The relation between the sputtering and the pressure of the residual gas is of special interest. Kohlschutter gives a hyperbolic curve for the pressure-sputtering relation, although he is of the opinion that the pressure plays a secondary role in the phenomenon. Gunthersültze (*ibid.*) also arrives at a hyperbolic relation. He starts with the assumption that the sputtered particles form a pseudo-gas with a partial pressure p_x at the cathode and zero at the anode. It seems that the above results hold only for a limited range of pressure variation out of the range of the pressure for which a self sustained discharge can be maintained. For when the pressure of the residual gas becomes sufficiently small, the number of ions impinging on the cathode may become proportionately small, *i.e.*, the current becomes more and more electronic. Now the sputtering depends directly on the number of ions impinging and also on the energy of the individual ions. Although the energy of the individual ions depends on the mean free path which varies inversely as the pressure, at the above mentioned pressures the scarcity of the ions may more than overbalance the increase in the energy of the individual ions. Consequently we should expect that up to a certain pressure a hyperbolic relation may hold but at pressures lower than this the sputtering should decrease with decrease of pressure. It was with a view to verify this effect that the following work was undertaken.

EXPERIMENTAL ARRANGEMENTS

In the following investigations, two sets of apparatus slightly different from each other were used, both proved to be equally useful.

In the first set a circular brass disc A (fig. 1), served as the anode. There was an annulus B for connecting to the pump and the vacuum indicator. Upon the brass

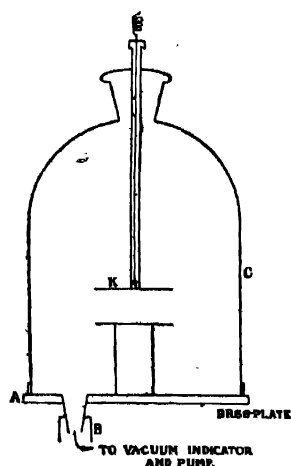


FIGURE 1.

plate was placed the bell jar C. Two different bell jars were used. The first was of capacity 3 litres and next a conical one with about a litre capacity. In this latter jar most of the quantitative work was carried out. Through the neck of the jars passed a glass tubing carrying in it the connecting lead to the cathode K which consisted of a rectangular or circular sheet of the experimental metal with a hook of the same metal revetted to it at the centre. It is held tight against the end of the glass tubing by means of a copper wire. At the other end of the tube was an ebonite bob, with a hole drilled through it through which passed the wire, and was sealed air tight with sealing wax.

In the second form represented in figure 2 the brass plate was replaced by a glass plate G, at the centre of which was drilled a hole, and through this hole passed the metallic connection to the anode which was a circular copper plate of 5 cm. diameter. The metallic connecting wire was joined to the glass plate by means of a glass cement made with the following ingredients:—

(1) Potassium silicate jelly	10 parts.
(2) Short Asbestos fibre	2 „
(3) Calcium fluoride	4 „
(4) Barium sulphate	1 part
(5) Glass powder	4 parts

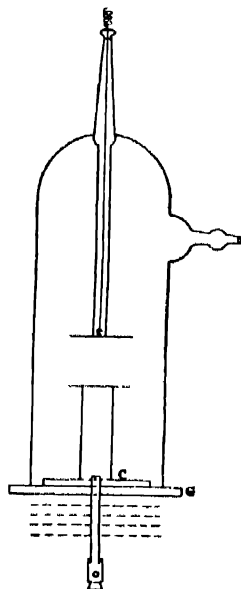


FIGURE 2.

The whole has to be ground together into a fine paste. The cement takes several days to dry ordinarily, but it can be heated to dry quickly. Outside the discharge tube was a radiator connected to the anode for cooling it. The bell jars of the

previous apparatus are now replaced by a tube worked into the form shown in the figure. The widest diameter is 6 cm., the wide end was ground on the glass plate containing the anode. Further, there is a side tube to it for making connections to the pump and the manometer.

The method of removing the tube from the glass plate needs a few words as the process is troublesome and is liable to cause the breakage of the tube. The method employed was to put a thick brass wire round the joint and heat the ends of the brass wire. The wax melted all round and the tube came off easily. Of course the pressure of the air inside was first equalized with that of the atmosphere.

Sealing. The temporary joint between the base and the upper vessel was sealed with a preparation of beeswax and rosin (half and half). This forms a very conveniently workable and efficient sealing wax. Other sealing agents such as plasticine and paraffine were used but these were found to be not so useful.

The interposed plates. Both for measuring the thickness of the deposit and for preparing the metallic films a glass plate had to be placed beneath the cathode. This was done by placing the glass plate on another glass plate usually of the same size, which in its turn was kept on a stand improvised by a piece of glass tubing about 1" diameter and of suitable height, different heights being used to obtain different distances between the cathode and the interposed plate.

The preparation of the plates. The plates were cut into squares of the required size (5 × 5 cm. approximately). These were boiled in sulphuric acid and potassium dichromate, washed with distilled water thoroughly and dried. Then a layer of collodion was applied to one of the faces of the glass plate; the layer was stripped on drying. This is done to remove all the dust from the surface. The treatment is essential both for obtaining a sufficiently strong film capable of being removed from the plate and also for weighing the deposit.

Drying agents. It is believed by some investigators, such as Derbyshire,⁴ that a drying agent is very necessary. In some of the experiments P_2O_5 was used. But it was found to be not so very indispensable.

Pump. A Cenco Hyvac pump was used for evacuating the sputtering vessel. A long glass tube of 50 cm. length and 3 cm. in diameter sealed at both ends to two narrow glass tubings, served very well as the container of calcium chloride, with glass wool packing at both ends, for drying. One end was connected to the pump through a stop cock, the other end had a T-connection communicating to the sputtering vessel and the manometer.

The manometer used was a kenometer after Dr. Redden and read up to 10^{-3} mm. pressure.

The High Tension Circuit consisted of a Ihrls transformer using 220 volts A.C. The maximum secondary voltage being 3,000 volts. The secondary current was rectified by means of a Lodge rectifier. A Ferranti milliammeter reading

up to 150 mA. and giving 2 mA. as the least scale division gave the current through the discharge vessel. The anode of the Lodge rectifier had to be cooled by means of a piece of wet rag. Figure 3 represents the essentials of the electrical circuit.

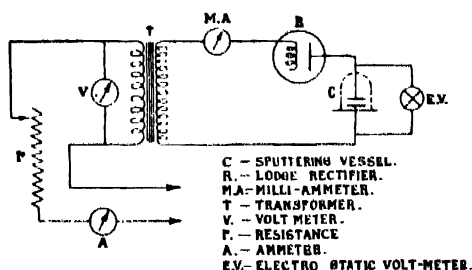


FIGURE 3.

The voltage across the discharge tube was estimated from that of the total secondary voltage after making an allowance for the potential fall through the rectifier.

QUANTITATIVE MEASUREMENT OF SPUTTERING OF Ag IN AIR

There are, besides other, two possibilities of investigating cathodic sputtering quantitatively. (1) by the loss of weight of the sputtered metallic cathode; (2) by allowing a part of the sputtered metal to be deposited on an interposed glass plate and then finding its thickness by weighing the deposit. In the earlier experiments both the loss of weight of the cathode and also the weight of the deposit were determined. The former was measured on a Sartorius balance weighing up to 1 mgm. Some investigators object to this method on the ground that the true loss cannot be found by this method. In the present case this method was given up partly for this reason and partly because it proved to be too tedious in the long run. While using the second method the deposit was weighed on a Paul Bunge microbalance. With this balance one can weigh accurately up to 0.01 mgm.

Variation of sputtering with time.

In order to verify the accuracy of the general measurement the relation between the sputtering and the time of discharge was investigated. The following table gives the readings. The deposit was expressed as the thickness of the metallic deposit I_d in $m\mu$. It was calculated by knowing the weight of the

deposit and the area of the plate assuming the deposit to be uniform, and taking the density to be the normal density. A correction to the area was applied in the cases of thick glass plates in which the edges of the plate were also covered. The area of the edges was added to the area of the upper face.

(1) The conical vessel was used. The distance between the cathode and the plate was kept equal to 4 cm. Area of the plate was about 25 sq. cm. The potential applied was approximately 2000 volts and the current through the discharge tube was 20 mA.

TABLE I

Time of experiment.	Thickness of the deposit in $m\mu$.
5 minutes	4
10 "	25.4
15 "	41.1
20 "	54.5
25 "	70.4
30 "	82.2

These readings are plotted in curve I (I_d against the time of exposure).

The same apparatus was used but with the distance between the cathode and the plate changed to 2.6 cms.

TABLE II

Time of exp	Press. of the gas in the discharge vessel.	Thickness of the deposit.
5 min.	178 mm.	37.4 $m\mu$
10 "	12 "	61.0
15 "	150 "	91.9
20 "	108 "	153.6

These are plotted in curve II (I_d against time of exposure).

These experiments were repeated again with another apparatus (described under the second set above). The voltage and the current were the same as before.

TABLE III

Time of exposure.	Pressure.	I_d , the thickness.
$2\frac{1}{2}$ min.	·186 mm.	15 $m\mu$
5 „	·156 „	22·7 „
$7\frac{1}{2}$ „	·132 „	30·0 „
10 „	·105 „	27·8 „
15 „	·132 „	61·0 „
25 „	·085 „	96·5 „

These are plotted in curve III (I_d against time).

In another set of readings it was noticed that a Ag cathode covered with oxide and other surface impurity and cleaned with sand paper, had to be given three and four successive exposures of 10 minutes' duration till the sputtering reached the normal value. The following table gives the values :—

Time of exposure is 10 minutes in each case.

The vessel is of 8 cm. diameter and the distance between the cathode and the plate is 3 cm.

Exposure.	Pressure.	I_d .
1st	·235 mm.	4·6 $m\mu$
2nd	·182 „	16 „
3rd	·216 „	20·2 „
4th	·199 „	25·3 „
5th	·217 „	41·2 „

It will be noticed that in spite of the difference of the pressure, the sputtering is continually increasing. This might have been caused by some greasy substance sticking to the cathode. The heating of the cathode while the discharge passed had the cleansing effect, hence the gradual increase. The first reading in table I is also low probably for exactly the same reason.

The points of each of the curves I, II, III, lie nearly on a straight line (as has been shown by previous workers). Some points are out as the pressure could not be kept strictly constant which markedly affects the sputtering.

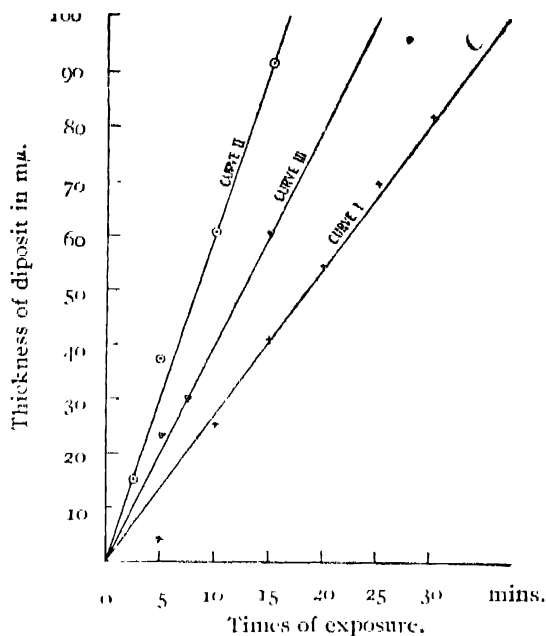


FIGURE 4.

Variation of Sputtering with Pressure

The following readings were taken by the method of the loss of weight of the cathode.

The current and the voltage were as before, 20 mA and 2,000 volts in each case. The pressure was measured by the kenometer the measurement being taken while the discharge was passing. The discharge was started after the evacuation reached equilibrium and the pump was kept running.

TABLE IV.

Pressure.	Loss of weight of the cathode in mg $\times 10$.
·285 mm.	28
·178 "	30
·168 "	31
·150 "	36
·136 "	35
·12 "	45
·117 "	44
·110 "	49
·105 "	43

These are plotted in curve IV.

Table V gives the same relation but measured by finding the thickness of a deposit I_s on a plate kept at a fixed position in the discharge vessel. Some of these readings are taken from those given in table III and reduced to 10 minutes exposure; others are added afterwards.

Table V

Pressure.	Thickness.
'340 mm.	18'1 m μ
'195 "	27'1 "
'179 "	31'0 "
'132 "	40 "
'115 "	45 "
'085 "	38'6 "

These are plotted in Curve V.

DISCUSSION OF THE RESULTS

Curves IV and V exhibit the expected effect. Both of them indicate that the sputtering is maximum for certain pressure.

In the case of curve IV it will be seen that some points do not lie exactly on the curve. This may be expected as the method used was "loss of weight of the cathode," which is rather rough, as has been already pointed out.

But the general agreement between the results obtained by the two methods is very prominent and it clearly brings out the suggested effect of pressure variation.

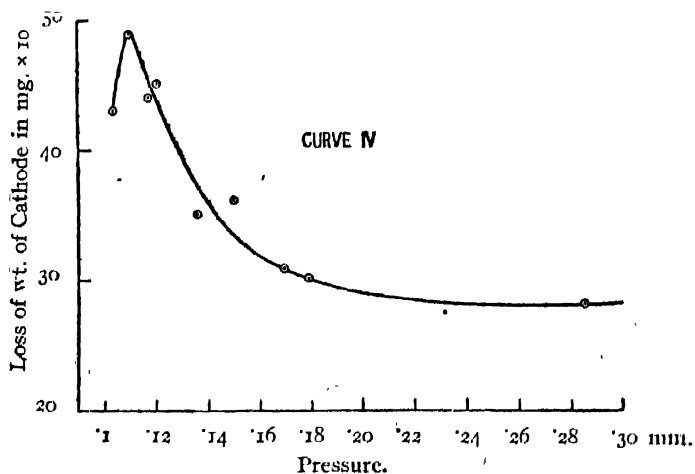


FIGURE 5.

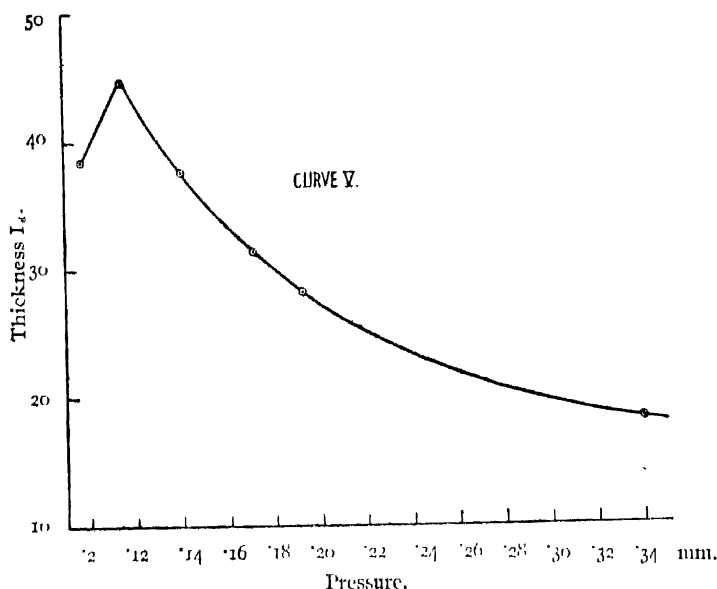


FIGURE 6.

On the right side of the maxima of the curve the run is similar to that obtained by Kohlschutter and Gunthersültze.

Zone formation on the plate

In experiments with the apparatus in which the conical glass jar was used, coloured zones in the deposited layer of the metal, of the type observed by Baum Blechschmidt and others were observed. These zones were circular although the cathode was rectangular. The radius of the circles were well defined and did not bear any definite relation to the cathode which was of rectangular shape. The mark on the cathode did not show any over sputtered circular region corresponding to the rings. The cathode was uniformly sputtered all over except in some cases in which a very narrow (about 1 mm.) border was left over all along the edges of the cathode. This is due to the end effect.

These zones lost their sharpness with varying distances from the cathode. Thus at a distance of 4 cm. from the cathode two exposures showed very beautiful rings, dark blue rings at the centre about 4 cm. in diameter. (The plate was about 5.5 cm. sq.). Then a border of violet, then yellow which extends right up to the corner. Near the middle of each side there is a further region of heavy deposit rather ill defined along the edges, a few mm. broad and running almost up to the corner.

When the distance between the cathode and the plate was decreased to 2.6 cm. the zone formation lost much of its definition, only a grey central thick

deposit of 4 cm. radius was formed, the sides being less thickly covered and the line of demarcation being fairly marked in reflected light. When the distance was further changed to 7 cm. there was hardly any zone formation. At greater distances from the cathode the distribution of the sputtered particles becomes more and more uniform due to the lateral diffusion and due to the collision of the particles amongst themselves and against the wall. Hence the deposit is uniform when the plate is kept at a great distance.

But as the distance between the cathode and the plate becomes smaller the condition becomes fairly complicated. The sputtered particles may not be uniformly distributed if we suppose that there is a preferential angular emission of sputtered particles from the cathode, as may be expected on the basis of the theory of accommodation as developed by Compton and Lamar,⁵ or again, there will be a different distribution if we accept the view of R. Seeliger and Sommermeyer⁶ that the emitted particles follow Kundser's Cosine law. Then there are other fast moving particles, namely, neutralized oxygen and nitrogen atoms moving perpendicular to the cathode and the plate surface and fast moving electrons also at right angles to the cathode surface; these particles most likely have an unequal density distribution in a plane parallel to that of the cathode. Now E. A. Johnson and L. Harris³ have shown that these particles disintegrate the deposit. Hence a deposit which might have been uniform otherwise may be made nonuniform by the preferential disintegration of certain parts.

The Sputtered particles as Pseudo-gas

In order to investigate the effect of interposing a screen between the "aufangplatte" and cathode the following arrangements were used. Upon the "aufangplatte" was placed a piece of glass tubing of diameter 1 cm. and height about 1.5 cm. and over this another glass plate of the same size as the "aufangplatte" was placed. The distance between the cathode and the "aufangplatte" being 4 cm.

It is found that in all cases there was a deposit on the lower plate along the edges. The width of the deposit was not regular.

The tube support for the upper glass plate is found to be heavily covered with silver. *The deposit being heaviest at the top.* These results are quite in accordance with the results obtained by A. London.⁷

This result strongly corroborates the formation of pseudo-gas of the sputtered particles (Kholschutter), especially the fact that the upper part of the supporting tube gets more heavily coated shows that the sputtered particles completely surround the upper plate and its stand and then condense upon the glass surface.

PREPARATION OF THIN METALLIC FILMS

The same apparatus was used for preparing thin metallic films, a glass plate prepared by the method already described is placed beneath the cathode at a distance just greater than the cathode dark space. In experiments so far performed it was found that the discharge must be abnormal. The exposure depends on the metal of the cathode ranging from a few minutes in the case of Ag to a few hours in the case of Al. The following table gives a rough idea of the relations. The voltage used was about 2,000.

Metal of Ca	Pressure.	Dark space.	Current.	Time of exp.	Remarks.
Cu	1-2 mm.	2 to 3 cm.	18 mA.	1-2½	very thin— 10^{-6}
	1 "	1 "		15 min.	thick dept Coloured—dull yellowish
Ag	1 "	1 "	20 "	5 min.	very thick
Ni			21 "	2 hrs	thick deposit
Fe	07 "		21 "	40 min.	thin yellowish
Al	07 "		20 "	4 hrs.	very thin

Some of these films were removed from the glass plate by the method after Thompson, namely, applying a *thin* layer of duco laquer and on drying peeling the metallic films off with the layer of the laquer. Then the metallic film is left on a strong Al base by dissolving the laquer off in a solvent.

ACKNOWLEDGMENT

In conclusion I take this opportunity to express my gratitude and sincere thanks to Dr. D. B. Deodhar, Reader in Physics, Lucknow University, under whom all this work was carried out and without whose help and keen interest the work would not have been possible. I should also like to thank the Lucknow University for giving me a reasearch fellowship which enabled me to carry out this investigation.

PHYSICS DEPARTMENT,
LUCKNOW UNIVERSITY.

REFERENCES

- ¹ Guntherschutze, *Z. f. Phys.*, **36**, 563 (1926).
- ² Blechschmidt, *Ann. der Phys.*, **81**, 999 (1926).
- ³ Jhonson and Harris, *Phys. Rev.*, **45**, 630 (1934).
- ⁴ Derbyshire, *Jour. Sc. Inst.*, **83** (1933).
- ⁵ Compton and Lamar, *Phys. Rev.*, **44**, 338 (1933).
- ⁶ R. Seeliger and Sommermeyer, *L. F., Phys. Rev.*, **93**, 692 (1935).
- ⁷ A London, *Phys. Rev.*, **11**, 40 (1900).

“ON THE THEORY OF A NON-LINEAR PARTIAL DIFFERENTIAL EQUATION OF THE ELLIPTIC-PERABOLIC TYPE”*

By M. RAZIUDDIN SIDDIQI

(Hyderabad—Deccan)

(Received for publication, March 25, 1938.)

ABSTRACT. The “Fourier Method” developed by the author for the unique solution of general non-linear equations of the parabolic and hyperbolic types has been extended to the non-linear partial differential equation of the elliptic-parabolic type

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial u}{\partial t} = u^2$$

and for certain boundary and initial conditions, unique solution has been obtained.

INTRODUCTION

Apart from the intrinsic interest of the subject, the occurrence of non-linear differential equations in modern physical theories, is making it imperative that such equations should be studied systematically. In several recent papers¹ the author has developed a “Fourier method” for the unique solution of general non-linear equations of the parabolic and hyperbolic types.

In this paper the method is extended to the non-linear partial differential equation of the elliptic-parabolic type

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial u}{\partial t} = u^2$$

for the boundary conditions:

$$u(0, y; t) = u(\pi, y; t) = 0; \quad u(x, 0, t) = u(x, \pi, t) = 0,$$

and the initial conditions

$$u(x, y; 0) = f(x, y) = \sum_{m,n} C_{m,n} \sin mx \sin ny.$$

* Communicated by the Indian Physical Society.

If it is assumed that $\sum (m^2 + n^2) |C_{m,n}| = C$, then it is proved that one

and only one regular solution $u(x, y; t)$ exists, which can be expressed in the form of a double Fourier series :

$$u(x, y; t) = \sum v_{m,n}(t) \sin mx \sin ny.$$

The coefficients $v_{m,n}(t)$ are determined with the help of a doubly infinite system of non-linear integral equations which is solved by the method of successive approximations.

It is found that there is no restriction on the value of t , which can extend to infinity. On the other hand, the given function $f(x, y)$ must be of a more restricted character, viz., such that C must not exceed a certain constant. This is in general the case for parabolic equations. For hyperbolic equations, the function f is more general, but the domain in t is more restricted.

EXISTENCE OF THE SOLUTION

We consider the differential equation

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} - \frac{\partial u}{\partial t} = u^2 \quad \dots (1)$$

and determine a solution $u(x, y, t)$ which is regular in the domain R defined by :

$$0 \leq x \leq \pi, 0 \leq y \leq \pi, 0 \leq t, \quad \dots (2)$$

and which satisfies the boundary conditions :

$$u(0, y; t) = u(\pi, y; t) = 0 \text{ for all } y \text{ and } t \text{ in } R, \quad \dots (3)$$

$$u(x, 0; t) = u(x, \pi; t) = 0 \text{ for all } x \text{ and } t \text{ in } R,$$

and

$$u(x, y; 0) = f(x, y) \text{ for all } x \text{ and } y \text{ in } R. \quad \dots (4)$$

We assume that $f(x, y)$ can be expanded in the double Fourier series :*

$$f(x, y) = \sum_{m,n}^* C_{m,n} \sin mx \sin ny, \quad \dots (5)$$

such that the series $\sum_{m,n} (m^2 + n^2) |C_{m,n}|$ is convergent.

* Unless otherwise stated, summation is to be extended from 1 to ∞ throughout this paper.

For the solution of (1) we write

$$u(x, y, t) = \sum_{m, n} v_{m, n}(t) \sin m x \sin n y, \quad \dots \quad (6)$$

and get

$$\begin{aligned} u^2(x, y, t) &= \sum_{m, n} \left\{ \frac{1}{\pi^2} \int_0^\pi \int_0^\pi u^2(\alpha, \beta; t) \sin m \alpha \sin n \beta d\alpha d\beta \right\} \sin m x \sin n y, \\ &= \sum_{m, n} Z_{m, n}(t) \sin m x \sin n y, \end{aligned} \quad \dots \quad (7)$$

where

$$Z_{m, n}(t) = \sum_{\substack{\kappa, \lambda, \\ \mu, \nu}} f_m(\kappa, \lambda) f_n(\mu, \nu) v_{\kappa, \mu}(t) v_{\lambda, \nu}(t), \quad \dots \quad (8)$$

with

$$\left. \begin{aligned} f_m(k, \lambda) &= \frac{2}{\pi} \int_0^\pi \sin k x \sin \lambda x \sin m x dx, \\ f_n(\mu, \nu) &= \frac{2}{\pi} \int_0^\pi \sin \mu y \sin \nu y \sin n y dy, \end{aligned} \right\} \quad \dots \quad (9)$$

From (1), (6) and (7) we get then

$$\begin{aligned} -\sum_{m, n} (m^2 + n^2) v_{m, n}(t) \sin m x \sin n y - \sum_{m, n} \frac{dv_{m, n}}{dt} \sin m x \sin n y \\ = \sum_{m, n} Z_{m, n}(t) \sin m x \sin n y; \end{aligned} \quad \dots \quad (10)$$

therefore for all $m, n \geq 1$,

$$\frac{dv_{m, n}}{dt} + (m^2 + n^2) v_{m, n}(t) = -Z_{m, n}(t). \quad \dots \quad (11)$$

We have assumed here, what we shall prove later, that all the series in (10) are absolutely and uniformly convergent in R .

From (4) and (5) we see that the solution (6) would have to satisfy the initial condition:

$$v_{m, n}(0) = C_{m, n} \quad (m, n = 1, 2, \dots) \quad \dots \quad (12)$$

The solution of (11) which satisfies the initial condition (12) is given by

$$v_{m, n}(t) = C_{m, n} e^{-(m^2 + n^2)t} - \int_0^t e^{-(m^2 + n^2)(t-s)} Z_{m, n}(s) ds$$

$$= C_{m,n} e^{-(m^2+n^2)t} - \int_0^t e^{-(m^2+n^2)(t-s)} \times \sum_{k\lambda\mu\nu} \frac{f_m(k,\lambda)}{(k^2+\mu^2)} \frac{f_n(\mu,\nu)}{(\lambda^2+\nu^2)} w_{k,\mu}(s) v_{\lambda,\nu}(s) ds. \quad (13)$$

We set for all $m, n \geq 1$:

$$w_{m,n}(t) = (m^2+n^2) v_{m,n}(t), \quad C'_{m,n} = (m^2+n^2) C_{m,n} \quad \dots \quad (14)$$

and get from (13)

$$w_{m,n}(t) = C'_{m,n} e^{-(m^2+n^2)t} - (m^2+n^2) \int_0^t e^{-(m^2+n^2)(t-s)} \times \sum_{k\lambda\mu\nu} \frac{f_m(k,\lambda)}{(k^2+\mu^2)} \frac{f_n(\mu,\nu)}{(\lambda^2+\nu^2)} w_{k,\mu}(s) v_{\lambda,\nu}(s) ds, \\ (m, n = 1, 2, \dots). \quad \dots \quad (15)$$

This is a doubly infinite system of non-linear integral equations for the determination of the functions $w_{m,n}(t)$ which in their turn determine the Fourier co-efficient $v_{m,n}(t)$.

We shall solve this system by the method of successive approximations, and for this purpose, we set

$$(0) \quad w_{m,n}(t) = C'_{m,n} e^{-(m^2+n^2)t} \quad \dots \quad (16)$$

and for all $r \geq 1$:

$$(r) \quad w_{m,n}(t) = C'_{m,n} e^{-(m^2+n^2)t} - (m^2+n^2) \int_0^t e^{-(m^2+n^2)(t-s)} \times \sum_{k\lambda\mu\nu} \frac{f_m(k,\lambda)}{(k^2+\mu^2)} \frac{f_n(\mu,\nu)}{(\lambda^2+\nu^2)} w_{k,\mu}^{(r-1)}(s) v_{\lambda,\nu}^{(r-1)}(s) ds \quad \dots \quad (17)$$

We have to prove the convergence of this approximation

We shall first show that the doubly infinite series

$$\sum_{m,n} \left| \frac{f_m(k,\lambda)}{(k^2+\mu^2)} \frac{f_n(\mu,\nu)}{(\lambda^2+\nu^2)} \right| \quad \dots \quad (18)$$

is uniformly convergent for all k, μ, λ, ν .

We have on writing $\Delta = \frac{d^2}{dx^2} + \frac{d^2}{dy^2}$

$$\sin mx \sin ny = - \frac{1}{(m^2 + n^2)} \Delta (\sin mx \sin ny),$$

Therefore

$$\begin{aligned} f_m(k, \lambda) f_n(\mu, \nu) &= - \frac{4}{(m^2 + n^2)\pi^2} \iint_0^\pi \sin kx \sin \mu y \sin \lambda x \sin \nu y \times \\ &\quad \Delta (\sin mx \sin ny) dx dy \\ &= - \frac{4}{(m^2 + n^2)\pi^2} \iint_0^\pi \sin mx \sin ny \\ &\quad \times \Delta (\sin kx \sin \mu y \sin \lambda x \sin \nu y) dx dy \\ &= - \frac{4}{(m^2 + n^2)\pi^2} \iint_0^\pi \sin mx \sin ny \left\{ -(k^2 + \lambda^2) \sin kx \sin \mu y \times \sin \lambda x \sin \nu y \right. \\ &\quad + 2k\lambda \cos kx \cos \lambda x \sin \mu y \sin \nu y - (\mu^2 + \nu^2) \sin kx \sin \mu y \sin \lambda x \sin \nu y \\ &\quad \left. + 2\mu\nu \sin kx \sin \lambda x \cos \mu y \cos \nu y \right\} dx dy. \end{aligned}$$

Therefore

$$\begin{aligned} \frac{|f_m(k, \lambda) f_n(\mu, \nu)|}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} &< \frac{4}{(m^2 + n^2)} \left\{ |f_m(k, \lambda) f_n(\mu, \nu)| + |g_m(k, \lambda) f_n(\mu, \nu)| \right. \\ &\quad \left. + |f_m(k, \lambda) g_n(\mu, \nu)| \right\} \quad \dots \quad (19) \end{aligned}$$

where

$$\left. \begin{aligned} g_m(k, \lambda) &= \frac{2}{\pi} \int_0^\pi \cos kx \cos \lambda x \sin mx dx, \\ g_n(\mu, \nu) &= \frac{2}{\pi} \int_0^\pi \cos \mu x \cos \nu x \sin nx dx. \end{aligned} \right\} \quad \dots \quad (20)$$

From Parseval's theorem we know that for all k, λ, μ, ν :

$$\sum_m f_m^2(k, \lambda) \leq 2, \quad \sum_n f_n^2(\mu, \nu) \leq 2,$$

$$\sum_m g_m^2(k, \lambda) \leq 2, \quad \sum_n g_n^2(\mu, \nu) \leq 2,$$

Therefore

$$\sum_{m,n} f_m^2(k, \lambda) f_n^2(\mu, \nu) \leq 4, \quad \sum_{m,n} g_m^2(k, \lambda) g_n^2(\mu, \nu) \leq 4,$$

$$\sum_{m,n} f_m^2(k, \lambda) g_n^2(\mu, \nu) \leq 4.$$

Thus from (19) we get on summing, squaring and using Schwarz's inequality as well as the inequality $2ab \geq a^2 + b^2$:

$$\begin{aligned} \left\{ \sum_{m,n} \frac{|f_m(k, \lambda) f_n(\mu, \nu)|}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \right\}^2 &< \left\{ \sum_{m,n} \frac{4}{m^2 + n^2} [|f_m(k, \lambda) f_n(\mu, \nu)| \right. \\ &\quad \left. + |g_m(k, \lambda) f_n(\mu, \nu)| + |f_m(k, \lambda) g_n(\mu, \nu)|] \right\}^2 \\ &\leq \sum_{m,n} \frac{16}{(m^2 + n^2)^2} \cdot \sum_{m,n} \left\{ |f_m(k, \lambda) f_n(\mu, \nu)| \right. \\ &\quad \left. + |g_m(k, \lambda) f_n(\mu, \nu)| + |f_m(k, \lambda) g_n(\mu, \nu)| \right\}^2 \\ &\leq \sum_{m,n} \frac{16 \times 3}{(m^2 + n^2)^2} \cdot \sum_{m,n} \left\{ f_m^2(k, \lambda) f_n^2(\mu, \nu) \right. \\ &\quad \left. + g_m^2(k, \lambda) f_n^2(\mu, \nu) + f_m^2(k, \lambda) g_n^2(\mu, \nu) \right\} \\ &< \sum_{m,n} \frac{16 \times 3 \times 12}{(m^2 + n^2)^2}. \end{aligned}$$

But the doubly infinite series $\sum_{m,n} \frac{1}{(m^2 + n^2)^2}$ is

convergent, so that $\left\{ \sum_{m,n} \frac{|f_m(k, \lambda) f_n(\mu, \nu)|}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \right\}^2$ and with it

the series (18) is uniformly convergent for all k, λ, μ, ν :

$$\sum_{m,n} \frac{|f_m(k, \lambda) f_n(\mu, \nu)|}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} = a \text{ (say)} \quad \dots \quad (21)$$

where a is an absolute constant.

We write, since $\sum_{m,n} (m^2 + n^2) C_{m,n}$ is supposed to be convergent,

$$\sum_{m,n} C_{m,n} = \sum_{m,n} (m^2 + n^2) C_{m,n} = C. \quad (22)$$

We have also for all $t > 0$ and all $m, n \geq 1$,

$$\begin{aligned} \left| \int_0^t e^{-(m^2+n^2)(t-s)} ds \right| &= \left| e^{-(m^2+n^2)t} \int_0^t e^{(m^2+n^2)s} ds \right| \\ &= \left| e^{-(m^2+n^2)t} \cdot \frac{e^{(m^2+n^2)t} - 1}{m^2 + n^2} \right| \leq \frac{1}{(m^2 + n^2)}. \end{aligned} \quad \dots (23)$$

Thus from (21) and (23) we get for all $t > 0$ and all $k, \lambda, \mu, \nu \geq 1$,

$$\begin{aligned} \sum_{m,n} (m^2 + n^2) \int_0^t e^{-(m^2+n^2)(t-s)} ds \cdot \frac{|f_m(k, \lambda) f_n(\mu, \nu)|}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \\ \leq \sum_{m,n} (m^2 + n^2) \cdot \frac{1}{(m^2 + n^2)} \cdot \frac{|f_m(k, \lambda) f_n(\mu, \nu)|}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \\ < a. \end{aligned} \quad \dots (24)$$

Thus if $\sum_{m,n} |\tau w_{m,n}^{(r-1)}(t)|$ converges uniformly for all t , we get from (17)

and (22) :

$$\sum_{m,n} \left| \tau w_{m,n}^{(r)}(t) \right| < C + a \left\{ \text{Max} \sum_{m,n} |\tau w_{m,n}^{(r-1)}(t)| \right\}^2 \quad \dots (25)$$

From (16) we get for all t

$$\sum_{m,n} |\tau w_{m,n}^{(0)}(t)| \times \infty \leq \sum_{m,n} C_{m,n} = C. \quad \dots (26)$$

Substituting this in (25) for $r=1$,

$$\sum_{m,n} |\tau w_{m,n}^{(1)}(t)| > C + aC^2.$$

We assume that

$$C < \frac{1}{4a}, \quad \dots (27)$$

so that we get

$$\sum_{m,n} \left| \tau w_{m,n}^{(1)}(t) \right| < C + C = 2C.$$

Substituting this again in (25) for $r=2$, we get for all t :

$$\sum_{m, n} \left| \frac{(2)}{w_{m, n}}(t) \right| < C + a(2C)^2 \\ < 2C.$$

In general, for all $r \geq 1$, and for all $t > 0$, we get

$$\sum_{m, n} \left| \frac{(r)}{w_{m, n}}(t) \right| < 2C. \quad \dots (28)$$

We shall prove further that the triple series

$$\sum_{r=0}^{\infty} \sum_{m, n} \left| \frac{(r+1)}{w_{m, n}}(t) - \frac{(r)}{w_{m, n}}(t) \right| \quad \dots (29)$$

converges uniformly for all t .

We have

$$\begin{aligned} \frac{(r+1)}{w_{m, n}}(t) - \frac{(r)}{w_{m, n}}(t) &= - (m^2 + n^2) \int_0^t e^{-(m^2 + n^2)(t-s)} \\ &\times \sum_{k, \lambda, \mu, \nu} \frac{f_m(k, \lambda) f_n(\mu, \nu)}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \left\{ \frac{(r)}{w_{k, \mu}}(s) - \frac{(r)}{w_{\lambda, \nu}}(s) - \frac{(r-1)}{w_{k, \mu}}(s) + \frac{(r-1)}{w_{\lambda, \nu}}(s) \right\} ds, \\ &= - (m^2 + n^2) \int_0^t e^{-(m^2 + n^2)(t-s)} \sum_{k, \lambda, \mu, \nu} \frac{f_m(k, \lambda) f_n(\mu, \nu)}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \\ &\times \left\{ \frac{(r)}{w_{k, \mu}}(s) \left[\frac{(r)}{w_{\lambda, \nu}}(s) - \frac{(r-1)}{w_{\lambda, \nu}}(s) \right] + \frac{(r-1)}{w_{\lambda, \nu}}(s) \left[\frac{(r)}{w_{k, \mu}}(s) - \frac{(r-1)}{w_{k, \mu}}(s) \right] \right\} ds. \end{aligned}$$

Therefore summing over m, n and taking account of (21) and (29) we get for all $t \geq 0$:

$$\sum_{m, n} \left| \frac{(r+1)}{w_{m, n}}(t) - \frac{(r)}{w_{m, n}}(t) \right| < a. 2. 2C \text{ Max } \sum_{m, n} \left| \frac{(r)}{w_{m, n}}(t) - \frac{(r-1)}{w_{m, n}}(t) \right| \quad \dots (30)$$

Repeating this reduction r times, we get for all $t > 0$:

$$\sum_{m, n} \left| \frac{(r+1)}{w_{m, n}}(t) - \frac{(r)}{w_{m, n}}(t) \right| < (4aC)^r \text{ Max } \sum_{m, n} \left| \frac{(1)}{w_{m, n}}(t) - \frac{(0)}{w_{m, n}}(t) \right| \quad \dots (31)$$

Now,

$$\begin{aligned} \frac{(1)}{w_{m, n}}(t) - \frac{(0)}{w_{m, n}}(t) &= - (m^2 + n^2) \int_0^t e^{-(m^2 + n^2)(t-s)} \\ &\times \sum_{k, \lambda, \mu, \nu} \frac{f_m(k, \lambda) f_n(\mu, \nu)}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \times \left[\frac{(1)}{w_{k, \mu}}(s) - \frac{(0)}{w_{k, \mu}}(s) \right] ds \end{aligned}$$

and $\sum_{m, n} \left| \frac{(o)}{w_{m, n}}(t) \right| \leq C$ for all t as shown in (26).

Therefore for all $t > 0$

$$\sum_{m, n} \left| \frac{(1)}{w_{m, n}}(t) - \frac{(o)}{w_{m, n}}(t) \right| < aC^2.$$

Consequently, we have from (31) on summing over r from 0 to ∞ , and remarking that in virtue of (27) $aC < 1$:

$$\begin{aligned} \sum_{r=0}^{\infty} \sum_{m, n} \left| \frac{(r+1)}{w_{m, n}}(t) - \frac{(r)}{w_{m, n}}(t) \right| &< aC^2 \sum_{r=0}^{\infty} (aC)^r \\ &< \frac{aC^2}{1-aC}. \end{aligned} \quad \dots (32)$$

This shows that the series (29) is uniformly convergent for all t .

From this we conclude that all the limits

$$\frac{w}{m, n}(t) = \lim_{r \rightarrow \infty} \frac{(r)}{w_{m, n}}(t) \quad (m, n = 1, 2, \dots) \quad \dots (33)$$

exist, and that $\frac{w}{m, n}(t)$ is continuous. Moreover, for all t :

$$\sum_{m, n} \left| \frac{w}{m, n}(t) \right| < 2C. \quad \dots (34)$$

From (17) on proceeding to $r \rightarrow \infty$, we get

$$\begin{aligned} \frac{w}{m, n}(t) &= \frac{C'}{m, n} e^{-(m^2+n^2)t} - (m^2+n^2) \int_0^t e^{-(m^2+n^2)(t-s)} \\ &\quad \sum_{k, \lambda, \mu, \nu} \frac{f_m(k, \lambda) f_n(\mu, \nu)}{(k^2+\mu^2)(\lambda^2+\nu^2)} \frac{w}{k, \mu}(s) \frac{w}{\lambda, \nu}(s) ds. \end{aligned} \quad \dots (35)$$

Writing again

$$\begin{aligned} v_{m, n}(t) &= \frac{1}{(m^2+n^2)} \frac{w}{m, n}(t), \\ \frac{C}{m, n} &= \frac{1}{(m^2+n^2)} \frac{C'}{m, n}, \end{aligned} \quad \dots (36)$$

we obtain

$$\begin{aligned} v_{m, n}(t) &= C \frac{1}{m, n} e^{-(m^2+n^2)t} \\ &\quad - \int_0^t e^{-(m^2+n^2)(t-s)} \sum_{k, \lambda, \mu, \nu} f_m(k, \lambda) f_n(\mu, \nu) \cdot \frac{v}{k, \mu}(s) \frac{v}{\lambda, \nu}(s) ds \end{aligned} \quad \dots (37)$$

Thus for all $m, n \geq 1$, $v_{m, n}(t)$ satisfies the integral equation (13) and consequently the differential equation (11).

We have proved in (34) that $\sum_{m,n} |\bar{w}_{m,n}(t)| = \sum_{m,n} (m^2 + n^2) |v_{m,n}(t)|$ is uniformly convergent; we also find that $\sum_{m,n} |Z_{m,n}(t)|$ is also uniformly convergent. We conclude from (11) that $\sum_{m,n} \left| \frac{d v_{m,n}}{dt} \right|$ is uniformly convergent. Thus we have shown that all the series in (10) are absolutely and uniformly convergent in R .

The function

$$u(x, y; t) = \sum_{m,n} v_{m,n}(t) \sin mx \sin ny \quad \dots (38)$$

is therefore the required solution of the equation (1) which satisfies the conditions (3) and (4).

We have to prove now that this is the only solution of its kind. Obviously, it is enough for this purpose to show that the system of integral equation (15) has no other solution than (33), which is such that (34) is also satisfied.

If possible, suppose that (15) has another solution $\bar{w}_{m,n}(t)$ ($m, n = 1, 2, \dots$) and that $\sum_{m,n} |\bar{w}_{m,n}^{(r)}(t)| < 2C$. \dots (39)

Then we have :

$$\begin{aligned} \bar{w}_{m,n}^{(r)}(t) - w_{m,n}^{(r)}(t) &= -(m^2 + n^2) \int_0^t -(m^2 + n^2)(t-s) \\ &\quad \sum_{k,\lambda,\mu,\nu} \frac{f_m(k,\lambda) f_n(\mu,\nu)}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \left\{ \bar{w}_{k,\mu}(s) \bar{w}_{\lambda,\nu}(s) - w_{k,\mu}^{(r-1)}(s) w_{\lambda,\nu}^{(r-1)}(s) \right\} ds \\ &= -(m^2 + n^2) \int_0^t -(m^2 + n^2)(t-s) \sum_{k,\lambda,\mu,\nu} \frac{f_m(k,\lambda) f_n(\mu,\nu)}{(k^2 + \mu^2)(\lambda^2 + \nu^2)} \\ &\quad \left\{ \bar{w}_{k,\mu}(s) \left[\bar{w}_{\lambda,\nu}(s) - w_{\lambda,\nu}^{(r-1)}(s) \right] + w_{\lambda,\nu}^{(r-1)}(s) \left[\bar{w}_{k,\mu}(s) - w_{k,\mu}^{(r-1)}(s) \right] \right\} ds. \end{aligned}$$

Then on account of (21), (28) and (39) we have for all t :

$$\sum_{m,n} \left| \bar{w}_{m,n}^{(r)}(t) - w_{m,n}^{(r)}(t) \right| < (a \cdot 2 \cdot 2C) \cdot \text{Max} \sum_{m,n} \left| \bar{w}_{m,n}^{(r-1)}(t) - w_{m,n}^{(r-1)}(t) \right|. \quad \dots (40)$$

Repeating this reduction r -times we get

$$\sum_{m,n} \left| \bar{w}_{m,n}^{(r)}(t) - w_{m,n}^{(r)}(t) \right| < (a \cdot 2C)^r \cdot \text{Max} \sum_{m,n} \left| \bar{w}_{m,n}^{(0)}(t) - w_{m,n}^{(0)}(t) \right|. \quad \dots (41)$$

ON THE TOTAL REFLECTION OF ELECTROMAGNETIC WAVES IN THE IONOSPHERE

By S. N. BOSE,
Dacca University.

(Received for publication, April 5, 1938.)

The conditions under which the electro magnetic waves get totally reflected in the upper atmosphere appear still worth a closer investigation. The usual procedure has been to attribute to the medium a refractive index which is calculated according to the classical method of Lorentz from the mechanical equation of motion of electrons. In an absorbing medium, this refractive index is a complex quantity, and depends not only on the properties of the medium but also on the frequency of the waves : as progressive waves through the ionosphere are damped, the co-efficient of damping will also enter into the expression of the refractive index. The usual Appleton-Hartree condition for total reflexion has been deduced by neglecting the damping, as a first approximation, and by putting the refractive index equal to zero. Discussion of the conditions when the damping is not negligible, gets very complicated indeed. certain workers in Allahabad, have suggested the further condition, that the group-velocity of the wave-train is zero, when total reflection takes place. This is a reasonable hypothesis, but the method by which the group-velocity is calculated neglects damping, an essential factor in the physical process. It appears also that the calculation of the group-velocity of waves in an absorbing medium is not amenable to the ordinary methods unless the damping is negligible, an approximation, which as has been already pointed out does not seem to agree closely with experience. It seems therefore necessary to change the method of analysis and to take instead of the equations of Maxwell with a complex refractive-index, the microscopic equations of Lorentz as basis for calculation. The method sketched here is a general one, suitable for problems of refractive-index of material media, as well as for discussion of propagation of waves in the ionosphere. It seems further amenable to modifications to suit the requirements of modern wave mechanics.

We take the familiar equations of Lorentz

$$\frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} - \text{Curl } \mathbf{H} = - \frac{\rho \mathbf{V}}{c} ; \quad \frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} + \text{curl } \mathbf{E} = 0.$$

$$\operatorname{div} \mathbf{E} = \rho, \quad \text{and} \quad \operatorname{div} \mathbf{H} = 0.$$

The density and the convection current, ρ and $\rho\mathbf{V}$, can be regarded as decomposable into two parts ρ_+ , and ρ_- and $(\rho\mathbf{V})_+$ and $(\rho\mathbf{V})_-$, respectively, which thus takes account of the corpuscular distribution of positive and negative charges. A wave disturbance in the medium can be considered by putting

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}e^{\mathbf{S}}, \quad \mathbf{H} = \mathbf{H}_0 + \mathbf{H}e^{\mathbf{S}}; \quad \rho_+ = \rho_+^0 + q_+e^{\mathbf{S}}, \quad \rho_- = \rho_-^0 + q_-e^{\mathbf{S}},$$

$\mathbf{V}_+ = \mathbf{V}_+^0 + \mathbf{W}_+e^{\mathbf{S}}$ and $\mathbf{V}_- = \mathbf{V}_-^0 + \mathbf{W}_-e^{\mathbf{S}}$, where the elements with 0 indices correspond to the undisturbed state of the medium. The convection current, and the electric-density become on this assumption equal to

$$\bar{\rho}\mathbf{V} = \rho_+ \mathbf{V}_+ + \rho_- \mathbf{V}_- = (\bar{\rho}\mathbf{V})_0 + \bar{\theta}e^{\mathbf{S}}$$

$$\text{where} \quad \bar{\theta} = [\rho_+^0 \mathbf{W}_+ + q_+ \mathbf{V}_+^0 + \rho_-^0 \mathbf{W}_- + q_- \mathbf{V}_-^0]$$

$$\text{and } \theta_0 = q_+ + q_-$$

Thus the components $(\theta_x, \theta_y, \theta_z)$ of the vector $\bar{\theta}$ correspond to the amplitudes of the fluctuating part of the convection current, and θ_0 , similarly to the fluctuating part of the electric density due to the disturbance.

The process is a familiar one: When S is a linear function of x, y, z, t , with a complex factor $2\pi i$, as is generally chosen for discussing monochromatic wave-propagation, $2\pi i S$ represents the phase of the disturbance and the surfaces for various values of S , represent the totality of all wave fronts as function of (x, y, z, t) . In order to tackle the more general case of a damped wave-train we shall not at first put any limitation to the form of S but shall assume it to be any function whatever, whose differential co-efficients may also have complex values. Removing the contributions on the both side of the equation by the various quantities corresponding to the undisturbed state, we get

$$\frac{1}{c} \frac{\partial}{\partial t} (\mathbf{E}e^{\mathbf{S}}) - \operatorname{curl} (\mathbf{H}e^{\mathbf{S}}) = - \frac{\theta}{c} e^{\mathbf{S}}$$

$$\frac{1}{c} \frac{\partial}{\partial t} (\mathbf{H}e^{\mathbf{S}}) + \operatorname{curl} (\mathbf{E}e^{\mathbf{S}}) = 0.$$

$$\operatorname{div} (\mathbf{E}e^{\mathbf{S}}) = \theta_0 e^{\mathbf{S}}, \quad \text{and} \quad \operatorname{div} (\mathbf{H}e^{\mathbf{S}}) = 0$$

We can also verify easily that

$$\operatorname{div} [\mathbf{E}e^{\mathbf{S}}] = [\operatorname{div} \mathbf{E} + (\operatorname{grad} S \cdot \mathbf{E})] e^{\mathbf{S}}$$

$$\operatorname{curl} [\mathbf{E}e^{\mathbf{S}}] = [\operatorname{curl} \mathbf{E} + \operatorname{grad} S \times \mathbf{E}] e^{\mathbf{S}}$$

$$\frac{d}{dt} \left[E e^S \right] = \left[\frac{dE}{dt} + E \frac{\partial S}{\partial t} \right] e^S$$

etc.

Under the usual conditions of propagation E , H representing the amplitudes of the electric and magnetic waves are slowly varying quantities whose differential co-efficients with regard to time and space co-ordinates can be neglected in comparison with the rapid variations of the function S , which represents the phase of the disturbance. We shall therefore put the differential co-efficients of E , H equal to zero, and thus get finally the equations reduced to the following form :—

$$\frac{1}{c} \frac{dS}{dt} E - (\text{grad } S \times H) = -\theta_1 c$$

$$\frac{1}{c} \frac{dS}{dt} H + (\text{grad } S \times E) = 0$$

$$(\text{grad } S \cdot E) = \theta_0$$

$$(\text{grad } S \cdot H) = 0$$

These can be regarded as the characteristic set of the wave-equations of Lorentz, and since there are eight equations, if $\frac{\partial S}{\partial x}$, $\frac{\partial S}{\partial y}$, $\frac{\partial S}{\partial z}$, $\frac{\partial S}{\partial t}$ are taken as unknown, certain compatibility conditions have further to be satisfied, which will give us the conditions under which wave-propagation can take place. We proceed to calculate these conditions by the usual method of vector-analysis. We have only to remember that, as the components of vectors may have complex-values, the geometrical interpretation of the various quantities may not be so immediate as in the usual cases : also a relation $\Lambda^2 = 0$, does not mean that the vector vanishes, as the components of the vector Λ_x , Λ_y , Λ_z need not be zero, when $\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 = 0$.

We shall call such vectors as singular, and in the problem that we have got before us, considerations of singular-vectors become important.

A few remarks regarding the geometrical interpretation of a singular vector may not be out-of-place ; regarding the components of a singular vector Λ , as decomposable into real and imaginary parts, we can always chose a real direction (λ, μ, ν) which is perpendicular to a complex-vector, viz., $(\Lambda_x + \Lambda_x^*, \dots)$

$$\text{i.e.,} \quad \text{such that} \quad \lambda \Lambda_x + \mu \Lambda_y + \nu \Lambda_z = 0$$

$$\lambda \Lambda_x^* + \mu \Lambda_y^* + \nu \Lambda_z^* = 0$$

i.e., an imaginary vector Λ , may be regarded as defining a real plane.

If co-ordinates are chosen so as to represent this plane, as the plane of (xy), a singular vector A , i.e., whose $A^2=0$, can be represented as

$(A, iA, 0)$ where A , may be a complex quantity, i.e., A is of the form $[\lambda + i\mu, -\mu + i\lambda, 0]$. Any vector perpendicular to a singular vector, will have in this co-ordinate system, the general form (P, iP, Q) where P and Q may be complex quantities. A non-singular vector, C perpendicular to A , will have $C^2 \neq 0$, i.e., $Q \neq 0$; a singular vector perpendicular to A , will also necessarily have $Q=0$, i.e., if A and B , are two singular vectors, both conditions $(A.B)=0$, and $(A \times B)=0$, may be satisfied at the same time and all singular vectors perpendicular to one another may be regarded as lying in one real plane.

If A and B are two perpendicular vectors of which one is singular while the other is not, any vector which is perpendicular to both A and B , must necessarily be singular, and will lie in the plane of A . This proposition follows immediately by writing out the general form of A and B in the manner explained above, and trying to write down the general form of C which satisfies the orthogonality condition. These preliminary remarks will be useful in discussing the singular case of total reflection, as we shall see later on. The other two relations in vector analysis which we shall have to use pretty frequently are

$$A.(B \times C) = B.(C \times A) = -B.(A \times C) = \text{etc.} \quad \dots (I)$$

$$\text{and} \quad A \times (B \times C) = B(AC) - C(AB) \quad \dots (II)$$

These have unrestricted validity even when the components of vectors have complex values, as they are formal identities, involving only re-arrangements of terms.

We shall at first deduce certain general conclusions from our equations

$$\frac{1}{c} \frac{\partial S}{\partial t} \quad \mathbf{E} - (\text{grad } S \times \mathbf{H}) = -\theta/c \quad \dots (1)$$

$$\frac{1}{c} \frac{\partial S}{\partial t} \quad \mathbf{H} + (\text{grad } S \times \mathbf{E}) = 0 \quad \dots (2)$$

$$(\text{grad } S, \mathbf{E}) = \theta_0 \quad \dots (3)$$

$$(\text{grad } S, \mathbf{H}) = 0 \quad \dots (4)$$

Scalar multiplication with $\text{grad } S$ of (1) gives, taking account of (3)

$$\frac{1}{c} \left[\frac{\partial S}{\partial t} \theta_0 + (\theta \text{ grad } S) \right] = 0 \quad \dots (A)$$

a relation which expresses the conservation of charge in the disturbed state of the medium.

Vector multiplication by grad S, of (2) gives

$$\frac{1}{c} \frac{\partial \tilde{S}}{\partial t} (\text{grad } S \times H) + \text{grad } S \times (\text{grad } S \times E) = 0$$

taking account of (1) we get

$$\frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 (\text{grad } S)^2 E + \frac{\theta}{c^2} \frac{dS}{dt} + \theta_0 \text{grad } S = 0 \quad (B)$$

$$\text{Scalar multiplication of (2) with } E \text{ gives} \quad (E \cdot H) = 0 \quad (C)$$

$$\text{Scalar multiplication (1) with } H \text{ gives} \quad (\theta H) = 0 \quad (D)$$

Relations (C), (D) and (4) show that the vectors E , θ , and grad S, are all in one plane perpendicular to H , also (1) shows that grad S, is perpendicular to $-\frac{\partial S}{\partial t} E + \theta$.

This vector can be regarded as representing the rate of change of induction, or $\frac{dD}{dt}$ of Maxwell's equation; thus H and D can be regarded as lying in the plane perpendicular to grad S while E and θ separately do not lie in it.

The arrangement of the various vectors thus agrees with our usual ideas about electromagnetic waves.

ENERGY AND MOMENTUM RELATIONS IN THE WAVE FIELD

Scalar multiplication of (1) and (2) by E and H respectively give,

$$\left[\frac{1}{c} \frac{\partial S}{\partial t} E^2 + \frac{(E \cdot \theta)}{c} \right] = E \cdot (\text{grad } S \times H) = -\text{grad } S [E \times H] \quad \dots (E)$$

$$\frac{1}{c} \frac{\partial S}{\partial t} H^2 = -\text{grad } S [E \times H] \quad \dots (F)$$

addition and subtraction of (E) and (F) give two further important relations

$$\frac{1}{c} \frac{\partial S}{\partial t} \frac{[E^2 + H^2]}{2} + \frac{(E \cdot \theta)}{2} = -\text{grad } S [E \times H] \quad \dots (G)$$

$$\frac{1}{c} \frac{\partial S}{\partial t} (E^2 - H^2) = -\frac{(E \cdot \theta)}{c}; \quad \dots (H)$$

also vector multiplication of (1), and (2) by H and E similarly gives

$$\frac{1}{c} \frac{\partial S}{\partial t} (E \times H) + H \times (\text{grad } S \times H) = -\frac{\theta \times H}{c}$$

or
$$\frac{1}{c} \frac{\partial S}{\partial t} (\mathbf{E} \times \mathbf{H}) + \mathbf{H}^2 \text{grad } S = - \frac{\theta \times \mathbf{H}}{c} \quad \dots \quad (\text{K})$$

also
$$\frac{1}{c} \frac{\partial S}{\partial t} (\mathbf{E} \times \mathbf{H}) + \mathbf{E}^2 \text{grad } S - \mathbf{E} (\text{grad } S \cdot \mathbf{E}) = 0$$

or
$$\frac{1}{c} \frac{\partial S}{\partial t} (\mathbf{E} \times \mathbf{H}) + \mathbf{E}^2 \text{grad } S = \theta_0 \mathbf{E}. \quad \dots \quad (\text{L})$$

Subtracting (L) from (K) we have

$$\text{grad } S (\mathbf{H}^2 - \mathbf{E}^2) = - \left[\theta_0 \mathbf{E} + \frac{\theta \times \mathbf{H}}{c} \right]. \quad (\text{M})$$

Multiplying (K) and by grad S,
we have the further relation

$$\frac{1}{c} \frac{\partial S}{\partial t} \cdot \text{grad } S [\mathbf{E} \times \mathbf{H}] + \text{grad } S \cdot \frac{(\theta \times \mathbf{H})}{c} = - \mathbf{H}^2 (\text{grad } S)^2$$

$$\frac{1}{c} \frac{\partial S}{\partial t} \text{grad } S [\mathbf{E} \times \mathbf{H}] = \theta_0^2 - (\text{grad } S)^2 \mathbf{E}^2,$$

but
$$\text{grad } S (\theta \times \mathbf{H}) = - \theta (\text{grad } S \times \mathbf{H}) = - \frac{1}{c} \left(\theta^2 + \frac{\partial S}{\partial t} (\mathbf{E} \cdot \theta) \right)$$

or
$$\frac{1}{c} \text{grad } S (\theta \times \mathbf{H}) = - \left[\frac{\theta^2}{c^2} + \frac{1}{c^2} \frac{\partial S}{\partial t} (\mathbf{E} \cdot \theta) \right].$$

These two relations thus become

$$\frac{1}{c} \frac{\partial S}{\partial t} \text{grad } S (\mathbf{E} \times \mathbf{H}) = + \frac{\theta^2}{c^2} + \frac{1}{c^2} \frac{\partial S}{\partial t} (\mathbf{E} \cdot \theta) - (\text{grad } S)^2 \mathbf{H}^2$$

$$\frac{1}{c} \frac{\partial S}{\partial t} \text{grad } S (\mathbf{E} \times \mathbf{H}) = - (\text{grad } S)^2 \mathbf{E}^2 + \theta_0^2.$$

From these we get

$$\frac{\theta^2}{c^2} - \theta_0^2 + \frac{1}{c^2} \frac{\partial S}{\partial t} (\mathbf{E} \cdot \theta) - (\text{grad } S)^2 (\mathbf{H}^2 - \mathbf{E}^2) = 0$$

or remembering (H) we see that

$$\left[\frac{1}{c^2} \left(\frac{\partial S}{\partial t} \right)^2 - (\text{grad } S)^2 \right] (\mathbf{H}^2 - \mathbf{E}^2) - S \theta_0^2 - \frac{\theta^2}{c^2} \quad \dots \quad (\text{P})$$

also $(\text{grad } S)^2 \mathbf{H}^2 = (\text{grad } S \cdot \mathbf{H})^2 + (\text{grad } S \times \mathbf{H})^2$

$$= \frac{1}{c^2} \left[\left(\frac{\partial S}{\partial t} \right)^2 \mathbf{E}^2 + 2 \frac{dS}{dt} (\mathbf{E} \cdot \theta) + \theta^2 \right]$$

we get

$$\begin{aligned} \frac{1}{c} \frac{\partial S}{\partial t} \text{grad } S (\mathbf{E} \times \mathbf{H}) &= -\frac{1}{c^2} \frac{\partial S}{\partial t} \left[\mathbf{E}^2 \frac{dS}{dt} + (\mathbf{E} \theta) \right. \\ &= \theta_0^2 - (\text{grad } S)^2 \mathbf{E}^2 \end{aligned} \quad (Q)$$

which can be written in the form

$$\left[\frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 - (\text{grad } S)^2 \right] \mathbf{E}^2 + \frac{(\mathbf{E} \theta)}{c^2} \frac{dS}{dt} + \theta_0^2 = 0 \quad (Q)$$

This equation could have been immediately deduced from (B) by taking scalar multiplication with $\vec{\mathbf{E}}$;

Equation (B)

$$\left[\frac{1}{c^2} \left(\frac{\partial S}{\partial t} \right)^2 - (\text{grad } S)^2 \right] \vec{\mathbf{E}} + \frac{\vec{\theta}}{c^2} \frac{dS}{dt} + \text{grad } S (\text{grad } S, \vec{\mathbf{E}}) = 0.$$

gives us generally the mutual disposition of $\vec{\mathbf{E}}$, $\vec{\theta}$ and $\text{grad } S$ when wave-propagation is possible, whereas the equation (Q) written in the form

$$\left[\frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 - (\text{grad } S)^2 \right] + \frac{1}{c^2} \frac{dS}{dt} \frac{(\mathbf{E} \theta)}{\mathbf{E}^2} + \frac{(\text{grad } S, \vec{\mathbf{E}})}{\mathbf{E}^2} = 0 \quad \dots (Q)$$

may be regarded as the equation for the refractive index, determining the velocity of propagation in any direction, prescribed by $\text{grad } S$.

THE NOTION OF THE REFRACTIVE-INDEX

A surface $S(x, y, z, t) = C$, may be regarded as moving perpendicular to itself with a velocity, given by

$$W = \frac{\frac{dS}{dt}}{|\text{grad } S|}$$

the refractive index, can be defined as $\frac{c}{W} = \mu = \frac{(\text{grad } S)}{\frac{1}{c} \frac{\partial S}{\partial t}}$ agreeing with our

usual definition, which however can be complex in the general case.

Introducing μ , equation (Q), can be written in the form

$$(1 - \mu^2) + \frac{(\mathbf{E} \theta)}{\mathbf{E}^2} \left/ \frac{dS}{dt} + \frac{c^2 (\text{grad } S, \vec{\mathbf{E}})^2}{\mathbf{E}^2} \right/ \left(\frac{dS}{dt} \right)^2 = 0.$$

ON RELATION BETWEEN θ AND $\mathbf{E}$

Early in the paper we have expressed θ , in terms of motion of the positive and negative charges, namely,

$$\theta = [\rho_0^+ W_0^+ + q^+ V_0^+ + \rho_0^- W_0^- + q^- V_0^-]$$

These involve in general both the original distribution of the charges, their velocities, as well as the amplitudes of velocities, and densities of positive and negative electricity due to the disturbance in the medium.

From general considerations, we can express the relation of θ , and $\mathbf{E}$ in the following way.

We have seen that during propagation of disturbance both θ and $\mathbf{E}$ lie in the plane perpendicular to $\mathbf{H}$. Therefore, θ can be decomposed into two components, one along $\mathbf{E}$, and another perpendicular to $\mathbf{E}$, in this plane, i. e., in the direction of $(\mathbf{E} \times \mathbf{H})$.

$$\theta \text{ thus can be put as equal to } \alpha \mathbf{E} + \beta \frac{[\mathbf{E} \times \mathbf{H}]}{|\mathbf{E}|}$$

$$\therefore (\theta \mathbf{E}) = \alpha \mathbf{E}^2, \quad \theta \times \mathbf{E} = \beta \frac{\mathbf{E}^2}{|\mathbf{E}|} \mathbf{H}$$

also from equations of wave-propagation

$$\theta \times \mathbf{E} = c \mathbf{H} (\text{grad } S \cdot \mathbf{E}) \quad \text{or} \quad \beta^2 / c^2 = \theta_0^2 / \mathbf{E}^2.$$

Writing therefore

$$\theta = \alpha \mathbf{E} + \beta \frac{[\mathbf{E} \times \mathbf{H}]}{|\mathbf{E}|}$$

we see that

$$\alpha = \frac{(\mathbf{E} \cdot \theta)}{\mathbf{E}^2}, \quad \beta = \frac{c \theta_0}{|\mathbf{E}|}$$

So that the refractive-index equation can be expressed in terms, of α and β ; in the form

$$(1 - \mu^2) + \frac{\alpha}{dS/dt} + \frac{\beta^2}{(dS/dt)^2} = 0.$$

Further,

$$\theta^2 = \alpha^2 \mathbf{E}^2 + \beta^2 \mathbf{H}^2$$

as the vectors $\mathbf{E}$ and $\mathbf{H}$ are perpendicular to one another it follows that, α and β , are two co-efficients which stand in very simple relation to the total polarisation current; α and β however are not constants but may involve $\text{grad } S$, as well as $\frac{dS}{dt}$, i.e., may be function of direction, and frequency of the waves.

CONDITION FOR TOTAL REFLECTION

It is well-known that for electro-magnetic waves in vacuum we have $E^2 - H^2 = 0$, as well as $(E \cdot H) = 0$. For waves in material media however $E^2 - H^2 \neq 0$, but $(E \cdot H) = 0$ remains still valid. The ratio of the electric and magnetic vectors depends generally upon the properties of the medium, as well as on the frequency of the wave and we can express this fact, by the relation (H) and (M)

$$\text{which are} \quad \frac{1}{c} \frac{\partial S}{\partial t} (E^2 - H^2) = - \frac{(E \cdot \theta)}{c}$$

$$\text{grad } S (H^2 - E^2) = - E = - \left(E \theta_0 + \frac{\theta \times H}{c} \right).$$

The ratio of the amplitudes of the vectors, H^2/E^2 , can therefore be expressed by the following relations :

$$\frac{dS}{dt} + \frac{(E \cdot \theta)}{E^2} = \frac{H^2}{E^2} \frac{dS}{dt}$$

$$\text{grad } S - \frac{E}{E^2} = \frac{H^2}{E^2} \text{grad } S,$$

depending upon the property of the medium, and the direction of disposition of the vector E , $\frac{(E \cdot \theta)}{E^2}$ will generally vary with $\frac{dS}{dt}$, as well as with grad S .

If however, $\frac{dS}{dt}$ tends to such a value that $\frac{\partial S}{\partial t} + \frac{E \cdot \theta}{E^2} = 0$, it follows that the vector $H^2 = 0$ ($E \neq 0$) independent of the amplitude of the wave traversing the medium ; the disturbance in such a case loses its wave-character, so that we can say the wave cannot penetrate beyond that region, and gets totally reflected ; we shall therefore take this condition $\frac{H^2}{E^2} = 0$, or an equivalent condition as characterising the condition of total reflection, and we can also correlate it with another physical idea.

We have also proved the following relation (F)

$$\frac{1}{c} \frac{\partial S}{\partial t} H^2 = - \text{grad } S [E \times H]$$

and also

$$\frac{1}{c} \frac{\partial S}{\partial t} \left[\frac{E^2}{2} + \frac{H^2}{2} \right] + \frac{E \cdot \theta}{2c} = - \text{grad } S (E \times H)$$

grad $S (E \times H)$ may thus be regarded as proportional to the flow of energy across the surface $S = \text{constant}$, so that grad $S (E \times H) = 0$ may be interpreted

to mean that the flow of energy across the wave-front vanishes. This agrees with our usual idea of total-reflection, at a boundary of two media, where the energy flows along the boundary interface in the limiting case.

We have also seen that

$$\frac{|\text{grad } S|}{\frac{1}{c} \frac{\partial S}{\partial t}} = \mu = \text{the refractive index of the medium,}$$

$$\begin{aligned} \text{from (2) we have } \frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 H^2 &= (\text{grad } S \times E)^2 = E^2 (\text{grad } S)^2 - (\text{grad } S \cdot E)^2 \\ &= -\frac{1}{c} \frac{dS}{dt} \text{grad } S [E \times H], \end{aligned}$$

we have

$$\frac{H^2}{E^2} = \frac{(\text{grad } S)^2}{\frac{1}{c^2} \left(\frac{dS}{dt} \right)^2} - \frac{(\text{grad } S \cdot E)^2}{E^2 \frac{1}{c^2} \left(\frac{dS}{dt} \right)^2} = -\frac{\text{grad } S [E \times H]}{\frac{1}{c} \frac{dS}{dt} E^2}; = -\frac{H(\text{grad } S \times E)}{\frac{1}{c} \frac{dS}{dt} E^2}.$$

In case $(\text{grad } S \cdot E) = 0$, we see that condition $\frac{H^2}{E^2} = 0$, is equivalent to the condition $\mu^2 = 0$, as has been assumed by Appleton to characterise the case of total reflection. If we now examine the condition (B) which gives the relation between the vectors E , θ and $\text{grad } S$, the condition $\theta = 0$ will mean, that the wave is propagated under such conditions that the vector E is parallel to θ .

Multiplying (1) with E , we have

$$\begin{aligned} E \times \theta &= c E \times (\text{grad } S \times H) \\ &= -c H (\text{grad } S \cdot E) \end{aligned}$$

so that $(\text{grad } S \cdot E) = 0$ will mean $E \times \theta = 0$, i.e., E is parallel to θ .

We thus see that if the wave is such that E is $\parallel$ to θ the condition of total reflection $H = 0$, or $\text{grad } S (E \times H) = 0$ is equivalent to the assumption $\mu = 0$; in the general case of wave propagation when E is not parallel to θ we would expect on the other hand the condition $H^2 = 0$ as giving a new result.

$H^2 = 0$, or $\text{grad } S (E \times H) = 0$, may be regarded as equivalent to the assumption that the group-velocity vanishes. The condition of total-reflection

postulated above is obviously suitable for a train of damped waves, because our analysis is general and the condition of non-penetrability has been deduced independent of all ideas of frequency.

We shall now apply the results of our analysis, in the particular case of the ionosphere.

The contribution of the positive charges, as well as of the bound electrons in θ , may be easily seen to be negligible in comparison with the contribution of the free electrons.

We can assume for the ionosphere

$$\theta = [\rho_0^- W^- + q^- V_0^-]$$

where these quantities refer only to the free-electrons present. If we average over a volume containing a large number of electrons, but small compared with the wave-length of the disturbance

$$\rho_0^- = Nc; \quad \theta = \overline{NcW};$$

the average value of the second term $q \overline{V_0^-}$, may be regarded as zero as the initial velocities of the charges, may be regarded as distributed chaotically in all directions.

Writing the equation of motion of a free electron after Lorentz as

$$m\ddot{x} + g\dot{x} = c \left[\dot{L}_x + \frac{v_y h_z - v_z h_y}{c} \right], \quad \text{etc.}$$

where (h_x, h_y, h_z) may be regarded as the components of a steady magnetic force, we have, dividing by m and multiplying by $\rho = Nc$, and averaging, the following equation

$$\dot{\theta} + \frac{g}{m} \theta = \frac{Nc^2}{m} \dot{L}_x + \left(\theta \times \frac{ch}{cm} \right)$$

where $(\theta_x = \overline{Nc v_x}, \text{ etc.})$.

Remembering that for a oscillatory disturbance $\dot{\theta} = \theta \frac{\partial S}{\partial t} e^S$ as before also that the other terms in the equation varies at e^S , the equation can be written as

$$\left(\frac{dS}{dt} + \frac{g}{m} \right) \theta = \frac{Nc^2}{m} \dot{L}_x + \left(\theta \times \frac{ch}{cm} \right) \quad \dots (Z)$$

Cancelling out e^S .

$\frac{g}{m} = \nu$ is usually called the collision frequency of the electrons.

We shall use this equation (Z) to calculate $\frac{(\mathbf{\hat{I}}\theta)}{\mathbf{\hat{I}}^2}$ or $\frac{\tilde{\theta}}{\mathbf{\hat{I}}}$.

Case I : This can be regarded as decomposable into two subcases.

(a) When $\frac{\theta \times ch}{cm} = 0$, i.e., θ is parallel to the external magnetic field, equation (Z) shows that θ is then parallel to $\mathbf{\hat{I}}$,

and
$$\frac{\mathbf{\hat{I}}\theta}{\mathbf{\hat{I}}^2} = \frac{\tilde{\theta}}{\mathbf{\hat{I}}} = Ne^2/m \left/ \left(\frac{dS}{dt} + v \right) \right.$$

the equation for determining the critical frequency for total reflection, becomes

$$\frac{dS}{dt} + \frac{Ne^2}{m} \left/ \left(\frac{dS}{dt} + v \right) \right. = 0$$

or
$$\left(\frac{dS}{dt} \right)^2 + v \left(\frac{dS}{dt} \right) + \frac{Ne^2}{m} = 0$$

or
$$\frac{dS}{dt} = -\frac{v}{2} \pm \sqrt{\frac{Ne^2}{m} - v^2/4}$$

This determines the dependence of the critical frequency on the ionic density; the train totally reflected is therefore of the form

$$e^{-v/2t} e^{\pm it \sqrt{Ne^2/m - v^2/4}}$$

or
$$w_c^2 = Ne^2/m - v^2/4$$

and the damping co-efficient is $v/2$

Case II : When $\theta \parallel \mathbf{\hat{I}}$ and $\theta^2 = 0$

that is the vector θ is singular, $\theta^2 = 0$ but $\theta \neq 0$

a vector $(\theta \times \frac{ch}{cm})$ will represent a vector parallel to θ , when h is non-singular and perpendicular to θ according to our former remarks about singular vectors. Choosing the direction of h , as the direction of Z , we can write the relation

$$\left(\frac{dS}{dt} + v \right) \theta = \frac{Ne^2}{m} \mathbf{\hat{I}} + \left(\theta \times \frac{ch}{cm} \right)$$

in the form

$$\begin{aligned} \left(\frac{dS}{dt} + v \right) \theta_x &= \frac{Nc^2}{m} E_x + \frac{ch}{cm} \theta_y \\ \left(\frac{dS}{dt} + v \right) \theta_y &= \frac{Nc^2}{m} E_y - \frac{ch}{cm} \theta_x \\ \text{or } \left(\frac{dS}{dt} + v \pm \epsilon \frac{ch}{cm} \right) (\theta_x \pm \epsilon \theta_y) &= \frac{Nc^2}{m} (E_x \pm \epsilon E_y) \\ \bar{\theta} \cdot \bar{E} &\text{ becomes equal to } \left[\frac{Nc^2/m}{\frac{dS}{dt} + v \pm \epsilon \frac{ch}{cm}} \right] \end{aligned}$$

according as θ and E are of the form $(A, \mp \epsilon A, 0)$.

The condition of total reflection now becomes, from (B)

$$\frac{dS}{dt} \left(\frac{dS}{dt} + v \pm \epsilon \frac{ch}{cm} \right) + \frac{Nc^2}{m} = 0$$

calling

$$\frac{dS}{dt} + v/2 \pm \epsilon \frac{ch}{2cm} = x$$

we have

$$x^2 + \frac{Nc}{m} - v^2/4 + \frac{c^2 h^2}{4c^2 m^2} \pm \frac{chv}{2cm} = 0$$

Solving the above equation, we find that the two reflected waves are circularly polarised and the critical frequencies are

$$\begin{aligned} \omega_{c\pm} &= \sqrt{\frac{Nc^2}{m} - v^2/4 + \frac{c^2 h^2}{4c^2 m^2} \mp \frac{ch}{2cm}} \\ T_{c\pm} &= v/2 \left[1 \pm \frac{ch}{2cm \omega'} \right] \text{ where } \omega' = \sqrt{\frac{Nc^2}{m} - v^2/4 + \frac{c^2 h^2}{4c^2 m^2}} \end{aligned}$$

So that when we have the critical frequency $= \frac{ch}{cm}$, i.e. $\omega' = \frac{ch}{2cm}$, one of the circularly polarised wave will be suppressed, and the other will be reflected with undiminished intensity: as this will necessarily mean $\frac{Nc^2}{m} = v^2/4$ the reflection of plane-polarised wave, discussed above in case I will not occur as the condition of total reflection gives $\omega_c = 0$, if $\frac{Nc^2}{m} = v^2/4$.

These two cases, correspond to the cases discussed by Appleton by putting $\mu = 0$ and the result agrees with the usual formula, when the collision-frequency is neglected.

Case III. When $\theta \neq E$:

We shall now calculate the value of $\frac{E \cdot \theta}{E^2}$ in the general case.

We have

$$\left(\frac{dS}{dt} + v \right) \theta = \frac{Ne^2}{m} E + \left(\theta \times \frac{eh}{cm} \right).$$

Scalar multiplication with E gives

$$\left(\frac{dS}{dt} + v \right) (E \cdot \theta) = \frac{Ne^2}{m} E^2 - \theta \cdot \left[E \times \frac{eh}{cm} \right];$$

also vector multiplication with E gives

$$\left(\frac{dS}{dt} + v \right) (E \times \theta) = \theta \cdot \left(E \cdot \frac{eh}{cm} \right) - \frac{eh}{cm} (E \cdot \theta).$$

Scalar multiplication by $\frac{ch}{cm}$ of the above relation gives

$$\left(\frac{dS}{dt} + v \right) \frac{ch}{cm} (E \times \theta) = \left(\frac{ch}{cm} \cdot \theta \right) \cdot \left(E \cdot \frac{ch}{cm} \right) - \left(\frac{ch}{cm} \right)^2 (E \cdot \theta).$$

Again, scalar multiplication of the original equation with $\frac{ch}{cm}$ gives

$$\left(\frac{dS}{dt} + v \right) \left(\frac{ch}{cm} \cdot \theta \right) = \frac{Ne^2}{m} \left(E \cdot \frac{ch}{cm} \right).$$

Combining (a), (b) and (c) we can easily deduce

$$\frac{(E \cdot \theta) \left[\left(\frac{dS}{dt} + v \right)^2 + \left(\frac{ch}{cm} \right)^2 \right]}{\left(\frac{dS}{dt} + v \right)} = \frac{\frac{Ne^2}{m} (E^2) \left[\left(\frac{dS}{dt} + v \right)^2 + \frac{1}{E^2} \left(E \cdot \frac{ch}{cm} \right)^2 \right]}{\left(\frac{dS}{dt} + v \right)^2}$$

$$\text{or } \frac{E \cdot \theta}{E^2} = Ne^2/m \frac{\left[\left(\frac{dS}{dt} + v \right)^2 + \frac{1}{E^2} \left(E \cdot \frac{ch}{cm} \right)^2 \right]}{\left(\frac{dS}{dt} + v \right) \left[\left(\frac{dS}{dt} + v \right)^2 + \left(\frac{ch}{cm} \right)^2 \right]}$$

when E and θ are non-singular vectors.

Now if we consider the case of total reflection as defined by $\text{grad } S \cdot [E \times H]$

$$= 0, [Q] \text{ gives } \frac{dS}{dt} = - \frac{(E \cdot \theta)}{E^2} \text{ as well as } \theta_0^2 - (\text{grad } S)^2 E = 0,$$

$\left(\mathbf{E}, \frac{e\mathbf{h}}{cm}\right)$ then becomes equal to $\frac{e}{cm} (\mathbf{E}_x h_x + i\mathbf{E}_y h_y)$

$$\mathbf{E}^2 = \mathbf{E}_x^2 - \mathbf{E}_y^2 \neq 0$$

$$\frac{1}{\mathbf{E}^2} \left(\mathbf{E}, \frac{e\mathbf{h}}{cm}\right)^2 = \frac{e^2}{c^2 m^2} \left[\frac{\mathbf{E}_x^2 h_x^2 - \mathbf{E}_y^2 h_y^2}{\mathbf{E}_x^2 - \mathbf{E}_y^2} + 2i h_x h_y \frac{\mathbf{E}_x \mathbf{E}_y}{\mathbf{E}_x^2 - \mathbf{E}_y^2} \right]$$

The frequency equation for the elliptically polarised beams would be

$$0 = \frac{dS}{dt} + \frac{Nc^2}{m} \left[\left(\frac{dS}{dt} + \nu \right)^2 + \frac{e^2}{c^2 m^2} \left[\frac{\mathbf{E}_x^2 h_x^2 - \mathbf{E}_y^2 h_y^2}{\mathbf{E}_x^2 - \mathbf{E}_y^2} + \frac{2i \mathbf{E}_x \mathbf{E}_y}{\mathbf{E}_x^2 - \mathbf{E}_y^2} h_x h_y \right] \right] ;$$

$$\left(\frac{dS}{dt} + \nu \right) \left[\left(\frac{dS}{dt} + \nu \right)^2 + \frac{e^2 h^2}{c^2 m^2} \right]$$

when the collision frequency is neglected this similarly becomes

$$\omega^2 = \frac{Nc^2}{m} \frac{\left[\omega^2 - \frac{e^2}{c^2 m^2} \left[\frac{\mathbf{E}_x^2 h_x^2 - \mathbf{E}_y^2 h_y^2}{\mathbf{E}_x^2 - \mathbf{E}_y^2} \right] \right]}{\omega^2 - e^2 h^2 / c^2 m^2} \quad \text{when} \quad \frac{\mathbf{E}_x \mathbf{E}_y}{\mathbf{E}_x^2 - \mathbf{E}_y^2} h_x h_y = 0.$$

This shows that the two cases, will be either $h_x = 0$, or $h_y = 0$

$$\omega^2 = \frac{Nc^2}{m} \frac{\left[\omega^2 - \frac{e^2 h_x^2 \mathbf{E}_x^2}{\mathbf{E}_x^2 - \mathbf{E}_y^2} \right]}{\omega^2 - \frac{e^2 h^2}{c^2 m^2}}, \quad \text{or} \quad \frac{Nc^2}{m} \frac{\left[\omega^2 + \frac{e^2}{c^2 m^2} \frac{h_y^2 \mathbf{E}_y^2}{(\mathbf{E}_x^2 - \mathbf{E}_y^2)} \right]}{\omega^2 - \frac{e^2 h^2}{c^2 m^2}}.$$

We have therefore

$$\omega^2 = \frac{Nc^2}{m} \frac{\left[\omega^2 + \frac{e^2 h^2}{c^2 m^2} \frac{\mathbf{E}_y^2}{\mathbf{E}_x^2 - \mathbf{E}_y^2} \cos^2 \alpha \right]}{\omega^2 - \frac{e^2 h^2}{c^2 m^2}}$$

when h is $\perp$ the major axis,

$$\text{or} \quad \omega^2 = \frac{Ne^2}{m} \frac{\left[\omega^2 - \frac{e^2 h^2}{c^2 m^2} \frac{\mathbf{E}_x^2 \cos^2 \alpha}{\mathbf{E}_x^2 - \mathbf{E}_y^2} \right]}{\omega^2 - \frac{e^2 h^2}{c^2 m^2}}$$

when h is $\perp$ to the minor axis,

Reflection of Electromagnetic Waves

Now also $\text{grad } S \cdot [\mathbf{E} \times \mathbf{H}]$ can be written in the form $H(\text{grad } S \times \mathbf{E})$, we that $\text{grad } S \parallel \mathbf{E}$

and
$$\frac{1}{E^2} \left(\mathbf{E}_1 \cdot \frac{c\mathbf{h}}{cm} \right)^2 = \frac{1}{(\text{grad } S)^2} \left(\text{grad } S \cdot \frac{c\mathbf{h}}{cm} \right)^2$$

$$\frac{1}{E^2} \left(\mathbf{E}_1 \cdot \frac{c\mathbf{h}}{cm} \right)^2 = \left(\frac{c\mathbf{h}}{cm} \right)^2 \cos^2 \alpha \text{ if grad } S \text{ is a vector whose compone}$$

have real ratios.

The relation $\frac{dS}{dt} + \frac{\mathbf{E} \cdot \boldsymbol{\theta}}{E^2} = 0$ becomes

$$\frac{dS}{dt} + \frac{\frac{Ne^2}{m} \left[\left(\frac{dS}{dt} + v \right)^2 + \frac{1}{E^2} \left(\mathbf{E}_1 \cdot \frac{c\mathbf{h}}{cm} \right)^2 \right]}{\left(\frac{dS}{dt} + v \right) \left[\left(\frac{dS}{dt} + v \right)^2 + \left(\frac{c\mathbf{h}}{cm} \right)^2 \right]}$$

If the disturbance is plane-polarised and the collision frequency is small we can put

$$v = 0, \quad \frac{1}{E^2} \left(\mathbf{E}_1 \cdot \frac{c\mathbf{h}}{cm} \right)^2 = \cos^2 \alpha \left(\frac{c\mathbf{h}}{cm} \right)^2$$

where α is the angle between the direction of propagation and the magnetic lines

The formula becomes, putting $\frac{dS}{dt} = i\omega$,

$$\omega_c^2 = \frac{\frac{Ne^2}{m} \left[\omega_c^2 - \left(\frac{c\mathbf{h}}{cm} \right)^2 \cos^2 \alpha \right]}{\omega_c^2 - \left(\frac{c\mathbf{h}}{cm} \right)^2}$$

agreeing with the formula supposed to be derived by putting group-velocity = zero by Bajpai and Mathur.¹

We shall have to remember however that $\mathbf{E}_1$ may be a complex-vector in the general case, any complex vector $\mathbf{E} = [E_x + iE_y, \text{ etc.}]$, may be regarded as perpendicular to a real direction, and choosing this direction as the direction of Z , we can choose as components of the complex vector, $(E_x, iE_y, 0)$ where x , and y are certain special directions and the external field is regarded as having components (h_x, h_y, h_z) in these special directions.

$$g(S) p(S) + \frac{Ne^2}{m} (\text{grad } S)^2 \pm v g(S) \frac{dS}{dt} - \frac{ch}{cm} = 0$$

or

$$\frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 - \text{grad}^2 S + \frac{Ne^2/mc^2 \left(\frac{dS}{dt} \right)^2}{\frac{dS}{dt} \left(\frac{dS}{dt} + v \pm v \frac{ch}{cm} \right)} = 0$$

which can again be put in the form

$$\frac{\mu^2}{c^2} \left(\frac{dS}{dt} \right)^2 - (\text{grad } S)^2 = 0.$$

If

$$\mu^2 = 1 + \frac{Ne^2/m}{\frac{dS}{dt} \left(\frac{dS}{dt} + v \pm v \frac{ch}{cm} \right)};$$

total reflection is obtained as before by putting $\mu = 0$

$\text{grad}^2 S$, can also become infinite, if $\frac{dS}{dt} = \pm \frac{vch}{cm} - v$
i.e., for a frequency equal to the gyromagnetic frequency.

Case III.

Neither

$$L(S) \text{ nor } \theta^2 = 0$$

i.e.,

$$\text{when } (\text{grad } S\theta) \neq 0$$

and θ is not parallel to E .

We have to proceed to further elimination to get the refractive index surface.

The elimination work becomes simplified if we choose a new set of axis, with Z , axis, in the direction of h .

The vector equation is now equivalent to the three scalar equations

$$L(S)\theta_x - g(S) \frac{dS}{dt} \theta_y - \frac{ch}{cm} = \frac{Ne^2}{m} S_x (S_x \theta_x + S_y \theta_y + S_z \theta_z) \quad \dots (i)$$

$$L(S)\theta_y + g(S) \frac{dS}{dt} \theta_x - \frac{ch}{cm} = \frac{Ne^2}{m} S_y (S_x \theta_x + S_y \theta_y + S_z \theta_z) \quad \dots (ii)$$

$$L(S)\theta_z = \frac{Ne^2}{m} S_z (S_x \theta_x + S_y \theta_y + S_z \theta_z) \quad \dots (iii)$$

where

$$\left(S_x = \frac{dS}{dx}, S_y = \frac{dS}{dy}, S_z = \frac{dS}{dz} \right).$$

$$\text{that grad } S \parallel L(S) p(S) + \frac{Ne^2}{m} (\text{grad } S)^2 \pm L(S) \frac{dS}{dt} - \frac{ch}{cm} = 0$$

$$c^2 \left(\frac{dS}{dt} \right)^2 - \left(\frac{dS}{dt} + v \right) \frac{dS}{dt} \text{grad}^2 S = 0^2 \quad \dots$$

$$\text{or} \quad \left(\frac{dS}{dx} \right)^2 + \left(\frac{dS}{dy} \right)^2 + \left(\frac{dS}{dz} \right)^2 = \frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 \frac{\frac{dS}{dt} \left(\frac{dS}{dt} + v \right) + \frac{Ne^2}{m}}{\frac{dS}{dt} \left(\frac{dS}{dt} + v \right)}$$

$$\text{or putting} \quad \left(\frac{dS}{dx} \right)^2 + \left(\frac{dS}{dy} \right)^2 + \left(\frac{dS}{dz} \right)^2 = \frac{\mu}{c^2} \left(\frac{dS}{dt} \right)^2$$

$$\mu^2 = 1 + \frac{Ne^2}{m} \left/ \frac{dS}{dt} \left(\frac{dS}{dt} + v \right) \right.$$

which agrees with the ordinary expression for the refractive index for plane polarised ordinary ray. The singular solution of the equation (1) when $p(S)$ and $(\text{grad } S) = 0$ gives the case of total reflection.

Case II. When $\theta^2 = 0$

$$(\theta \text{ grad } S) = 0.$$

The vector equation (R), can be satisfied only when

$$L(S) \theta - g(S) \frac{dS}{dt} \left(\theta \times \frac{ch}{cm} \right) = 0$$

i.e., when $\left(\theta \times \frac{ch}{cm} \right)$ becomes parallel to θ .

This same case, already discussed means that θ is perpendicular to h , and choosing a new set of perpendicular axis, with h in the direction of Z , we see $L(S)$, $p(S)$, $g(S)$ are invariants for orthogonal transformations. The vector equation can be split up into two equations

$$L(S) \theta_x - g(S) \frac{dS}{dt} \theta_y \frac{ch}{cm} = 0$$

$$L(S) \theta_y + g(S) \frac{dS}{dt} \theta_x \frac{ch}{cm} = 0.$$

So that remembering $\theta_x^2 + \theta_y^2 = 0$

$$\text{we have} \quad L^2(S) + g^2(S) \left(\frac{dS}{dt} \right)^2 \left(\frac{ch}{cm} \right)^2 = 0$$

which breaks up into two equations

From (i) and (ii) we easily get the relations

$$\begin{aligned} \theta_x \left[L^2(S) + g^2(S) \left(\frac{dS}{dt} \right)^2 \frac{c^2 h^2}{c^2 m^2} \right] \\ = \frac{Nc^2}{m} \left[L_x(S) S_x + S_y g(S) \frac{dS}{dt} \frac{ch}{cm} \right] (S_y \theta_x + S_y \theta_y + S_z \theta_z) \\ \theta_y \left[L^2(S) + g^2(S) \left(\frac{dS}{dt} \right)^2 \frac{c^2 h^2}{c^2 m^2} \right] \\ = \frac{Nc^2}{m} \left[L_y(S) S_y - S_x g(S) \frac{dS}{dt} \frac{ch}{cm} \right] [x \theta_x + S_y \theta_y + S_z \theta_z] \end{aligned}$$

and

$$I_z \theta_z = \frac{Nc^2}{m} S_z [S_x \theta_x + S_y \theta_y + S_z \theta_z]$$

$$\frac{\theta_x}{S_x \theta_x + S_y \theta_y + S_z \theta_z} = \frac{L_x(S) S_x + S_y g(S) \frac{dS}{dt} \frac{ch}{cm}}{L^2(S) + g^2(S) \left(\frac{dS}{dt} \right)^2 \frac{c^2 h^2}{c^2 m^2}} \cdot \frac{Nc^2}{m} \quad \dots (iv)$$

$$\frac{\theta_y}{S_x \theta_x + S_y \theta_y + S_z \theta_z} = \frac{L_y(S) S_y - S_x g(S) \frac{dS}{dt} \frac{ch}{cm}}{L^2(S) + g^2(S) \left(\frac{dS}{dt} \right)^2 \frac{c^2 h^2}{c^2 m^2}} \cdot \frac{Nc^2}{m} \quad \dots (v)$$

$$\frac{\theta_z}{S_x \theta_x + S_y \theta_y + S_z \theta_z} = \frac{\frac{Nc^2}{m} S_z}{L(S)} \quad \dots (vi)$$

multiplying (iv), (v) and (vi) by S_x , S_y , S_z we have

$$I = \frac{Nc^2}{m} \left[\frac{L(S) (S_x^2 + S_y^2)}{L^2(S) + g^2(S) \left(\frac{dS}{dt} \right)^2 \left(\frac{ch}{cm} \right)^2} + \frac{S_z^2}{L(S)} \right]$$

$$\begin{aligned} \text{or } L(S) \left[L^2(S) + g^2(S) \left(\frac{dS}{dt} \right)^2 \left(\frac{ch}{cm} \right)^2 \right] \\ = \frac{Nc^2}{m} \left[L^2(S) (S_x^2 + S_y^2 + S_z^2) + S_z^2 g^2(S) \left(\frac{dS}{dt} \right)^2 \left(\frac{ch}{cm} \right)^2 \right] \end{aligned}$$

now writing

$$S_s^2 = \text{grad}^2 S \cos^2 \alpha$$

where α = the angle between the wavenormal and the magnetic field, we have

$$L^2(S) \left[L(S) - \frac{Nc^2}{m} \text{grad}^2 S \right] + g^2(S) L(S) \left(\frac{dS}{dt} \right)^2 \left(\frac{eh}{cm} \right)^2 \\ - \frac{Nc^2}{m} \left(\frac{eh}{cm} \right)^2 g^2(S) \left(\frac{dS}{dt} \right)^2 \text{grad}^2 S \cos^2 \alpha$$

remembering $L(S) - \frac{Nc^2}{m} \text{grad}^2 S = p(S)g(S)$

and rejecting the factor $g(S)$ the equation finally assumes the form

$$p(S)L^2(S) + g(S) \left(\frac{dS}{dt} \right)^2 \left(\frac{eh}{cm} \right)^2 L(S) \\ - \frac{Nc^2}{m} \left(\frac{dS}{dt} \right)^2 g(S) \left(\frac{eh}{cm} \right)^2 \text{grad}^2 S \cos^2 \alpha = 0$$

when this equation is regarded as a quadratic in $(\text{grad}^2 S)$, i.e., when the value of $\frac{dS}{dt}$ is supposed to be prescribed, the two roots of $\text{grad}^2 S$, become, let us say

$f_1 \left(\frac{dS}{dt}, \alpha \right)$, and $f_2 \left(\frac{dS}{dt}, \alpha \right)$. So that we get two rays, corresponding to any prescribed α .

Corresponding to the two refractive indices

$$\mu_1^2 = \frac{f_1 \left\{ \frac{dS}{dt}, \alpha \right\}}{\frac{1}{c^2} \left\{ \frac{dS}{dt} \right\}^2}, \text{ and } \mu_2^2 = \frac{f_2 \left\{ \frac{dS}{dt}, \alpha \right\}}{\frac{1}{c^2} \left\{ \frac{dS}{dt} \right\}^2}$$

When damping is neglected, $\frac{dS}{dt} = i\omega$

We see from (iv), (v) and (vi), $\theta_x : \theta_y : \theta_z$

defines a complex-ratio, as $L(S)$ will become real, and $\frac{dS}{dt}$ pure imaginary, the two split rays will there be elliptically polarised, and the ratio of the axis, projected on a plane perpendicular of the magnetic field, is easily seen to be

$$\frac{g(S) \frac{dS}{dt} \frac{eh}{cm}}{L(S)} = \frac{g(S) \frac{dS}{dt} \left(\frac{eh}{cm} \right)}{\left[\frac{p(S)}{c^2} - \text{grad}^2 S \right]} = \frac{\left[\frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 - \text{grad}^2 S \right] \frac{eh}{cm}}{\frac{dS}{dt} \left[\frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 - \text{grad}^2 S + \frac{Nc^2}{mc^2} \left(\frac{dS}{dt} \right)^2 \right]};$$

for large values of $\text{grad}^2 S$ this tends to $\rightarrow \frac{ch}{cm\omega_c t}$;

Writing oft the equation in extenso, and putting $\text{grad}^2(S) \approx y$

We see the equation

$$0 = p(S) \left[\frac{p(S)}{c^2} \left(\frac{dS}{dt} \right)^2 - \frac{dS}{dt} \left(\frac{dS}{dt} + v \right) y \right]^2 + \left[\frac{1}{c^2} \left(\frac{dS}{dt} \right)^2 - y \right] \left(\frac{ch}{cm} \right)^2 \left(\frac{dS}{dt} \right)^2$$

$$\left\{ p(S) \left(\frac{dS}{dt} \right) - y \left(\frac{dS}{dt} + v \right) \frac{dS}{dt} + \frac{Nc^2}{m} \cos^2 \alpha \right\}$$

$$\text{The co-efficient of } y^2 = p(S) \frac{dS}{dt} \left(\frac{dS}{dt} + v \right)^2 \left(\frac{ch}{cm} \right)^2 \left(\frac{dS}{dt} \right)^2 \left[\frac{dS}{dt} \left(\frac{dS}{dt} + v \right) \right. \\ \left. + \frac{Nc^2}{m} \cos^2 \alpha \right]$$

The absolute term on the other hand is equal to

$$\frac{p^3(S)}{c^4} \left(\frac{dS}{dt} \right)^4 + \frac{1}{c^4} \left(\frac{dS}{dt} \right)^6 p(S) \left(\frac{ch}{cm} \right)^2 = p(S) \left(\frac{dS}{dt} \right)^4 \left[p^2(S) + \left(\frac{dS}{dt} \right)^2 \left(\frac{ch}{cm} \right)^2 \right]$$

We get therefore

$$\frac{dS}{dt} \left(\frac{dS}{dt} + v \right) + \frac{\frac{Nc^2}{m} \left[\left(\frac{dS}{dt} + v \right)^2 + \left(\frac{ch}{cm} \right)^2 \cos^2 \alpha \right]}{\left[\left(\frac{dS}{dt} + v \right)^2 + \left(\frac{ch}{cm} \right)^2 \right]} = 0$$

as defining the critical frequencies for total reflexion. This is in the general case when collision frequency is not neglected an equation of the fourth degree having two different conjugate complex roots corresponding to two elliptically polarised rays :

or when collision frequency is neglected,

$$\text{and} \quad \frac{dS}{dt} = \omega,$$

the above relation reduces to

$$\omega_c^2 = \frac{Nc^2}{m} \frac{\left[\omega^2 + \left(\frac{ch}{cm} \right)^2 \cos^2 \alpha \right]}{\omega^2 + \left(\frac{ch}{cm} \right)^2}$$

which agrees with the expression arrived at by Rai, Bajpai, and Mathur, and also with the result arrived at by another method.

From energy consideration, we have seen, that when $\mathbf{E} \parallel \theta$ the condition of total reflection $\text{grad } S [\mathbf{E} \times \mathbf{H}] = 0$, is satisfied $(\text{grad}' S)^2 = 0$: Here the propagation stops from penetrating further, as $\mathbf{H}$ vanishes, and the field beyond becomes electrostatic in character. When $(\text{grad } S \cdot \mathbf{E}) \neq 0$, which will happen when the direction of propagation makes an angle with the magnetic field, the electric vector, is not the wave front, and the total-reflection condition results when electric vector coincides with the wave normal. This happens as $(\text{grad } S)^2 \rightarrow \alpha$. The Poynting vector then lies in the wave front; The flow of energy across the surface stops, and the waves get totally reflected.

CONCLUSION

We have discussed the question of ionosphere at some length, but it will be easily seen, that the method can be applied with the same ease for discussion of propagation of light in a material medium. We have only to utilise the corresponding Lorentz-equation for motion of bound-electrons, which can be made to yield a relation similar to the equation (Z) deduced for the ionosphere. Readers interested in mathematical analysis will easily recognise the method as an application of the method of characteristics, used for discussions of wave-propagation by Hadamard, Debye, and others. So far as the writer is aware the method has not been applied to the microscopic equations of Lorentz, where however the extension does not seem to create any difficulty when the waves, are looked upon as possible modes of oscillation of the stationary electro-magnetic field, generated by positive and negative charges, present in the medium.

PHYSICAL LABORATORY,
Dacca.

REFERENCES

1. Bajpai, R. R. and Mathur, K. B., *Ind. J. Phys.*, **11**, 105 (1937).

ON THE HEAT CAPACITIES OF A FEW CRYSTALS AT LOW TEMPERATURES

By S. C. SIRKAR

AND

J. GUPTA.

(Received for publication, April 25, 1938.)

ABSTRACT. The heat capacities of crystals of ammonium chloride, carbon dioxide, sulphur and benzene observed at low temperatures have been examined in order to ascertain whether the observed values of C_p indicate the presence of the contributions of Debye functions corresponding to the new Raman lines in the low frequency region observed with these crystals. It has been found that in the case of ammonium chloride a Debye function corresponding to the line 183 cm^{-1} , and another Einstein function for the angular oscillations can explain satisfactorily the values of C_p observed at low temperatures. In the case of carbon dioxide and sulphur on the other hand, Einstein functions corresponding to the new lines, instead of Debye functions have to be taken into account in order to explain the observed values of C_p . In the case of benzene also, there is agreement between the observed and the calculated values of C_p if the Einstein functions corresponding to the new lines are taken into consideration. It is pointed out that the above fact as well as the selection rules for the appearance of Raman lines due to lattice oscillations, when applied to the crystals of benzene definitely lead to the conclusion that the new lines are not due to lattice oscillations in the case of benzene.

It is well known that the heat capacities of many crystals at low temperatures are not given by a Debye function alone even when the contributions of the Einstein functions due to the known intramolecular vibrations are quite negligible. It was pointed out by Pauling¹ that simple molecules, e.g., N_2 , O_2 , H_2 , CO , HCl , HBr , etc., execute angular oscillations about equilibrium orientations even at very low temperatures, and in some cases the molecules rotate freely in the solid state above some critical temperatures. As the frequencies of such oscillations are low, the corresponding Einstein functions contribute appreciably to the heat capacities at low temperatures, besides the Debye functions. The contribution of the Debye function to C_p can be easily calculated if the frequency of lattice oscillation be known. In the case of the substances mentioned above the frequencies of lattice oscillation were not known and therefore Pauling tried to calculate the values of ν , the frequencies of angular oscillation by assuming that the temperature at which the heat capacity reduces to 5 cal./mole.

per degree is equal to $\frac{h\nu}{3k}$ and the separate contributions of Debye and Einstein functions could not be calculated more accurately. In recent years, the study of the Raman spectra of solid substances having molecules more complicated than those discussed by Pauling has revealed the presence of new Raman lines with values of $\Delta\nu$ ranging from about 20 cm^{-1} up to about 190 cm^{-1} . Gross and Vuks² who first observed these new lines in the case of a few aromatic compounds suggested that the lines might be due to lattice oscillations. Such lines were observed by one of the present authors³ in the case of many substances in the solid state and at the temperature of liquid oxygen and those investigations have since been extended to a few organic and inorganic compounds by the present authors.⁴ It has also been pointed out by one of the present authors⁵ that strong new lines are observed in some cases even when lattice oscillations are forbidden in Raman effect according to selection rules. Recently, Venkateswaran⁶ has suggested that flexural oscillations of the lattice are responsible for the origin of the new Raman lines. Since the oscillations of different molecules have definite phase relations in the case of the flexural oscillation postulated by Venkateswaran, this oscillation is different from the angular oscillations of individual molecules postulated by Pauling, and should be treated as a lattice oscillation when its contribution to the heat capacity is considered. The object of the present paper is to discuss how far the observed heat capacities at low temperatures are explained by assuming that the new lines are due either to ordinary lattice oscillations or to the flexural oscillations of the lattice mentioned above.

AMMONIUM CHLORIDE

It may be of interest first to examine whether there is quantitative agreement between the observed heat capacities and those calculated in the case of the crystals for which the frequency of lattice oscillation is known. The crystals of ammonium chloride furnish a suitable example to be dealt with for this purpose, because it has been shown by Menzies and Mills⁷ by investigating the Raman spectra of these crystals, that the new line at 183 cm^{-1} which appears at temperatures below -30°C is due to lattice oscillation. It has already been pointed out by Pauling⁸ that since there is a catastrophic change in the heat capacity at about -30°C , probably the ammonium ions begin to rotate freely at this temperature and therefore at lower temperatures they are executing angular oscillations of small amplitudes about equilibrium orientations. These oscillations do not produce any appreciable change in polarisability in an isotropic ion like NH_4^+ , and so the Raman lines due to these oscillations are not observed. Also it has been shown by Menzies and Mills conclusively that the new line at 183 cm^{-1} is due to the oscillation of the lattice through the NH_4 ions against that through the Cl ions. The crystals

being cubic, the frequency of lattice oscillation is the same for all the three degrees of freedom and for the tetrahedral ammonium ion, the angular oscillation can also take place about all the three axes with the same frequency. The heat capacities are expected in this case to be given by the relation $C_p = 3RD(\theta/T) + 3RE(\theta'/T)$, where θ and θ' are respectively equal to $h\nu/k$ and $h\nu'/k$, ν and ν' being the frequencies of lattice and angular oscillations respectively. In this case ν may be assumed to be equal to 180 cm^{-1} , because though Menzies and Mills have observed that the frequency of this line does not alter appreciably with the lowering of temperature, it is expected to increase by 2 or 3 cm^{-1} at very low temperatures. The value of ν' is not known. It can be assumed however that at very low temperatures $3RE(\theta'/T) = C_p - 3RD(\theta/T)$ and if with the value of ν' calculated in this way for a particular temperature, the values of C_p calculated for other temperatures agree with the observed values, it may be concluded that the value of ν' so obtained is not far from the actual value. The calculated values of C_p with the assumption that $\theta = 266^{\circ}\cdot 5$ and $\theta' = 190^{\circ}$ are given in table I. It will be seen that there is fair agreement between these values and the observed values⁹ of C_p given in the last column up to 125°K .

TABLE I. NH_4Cl . $\theta = 266^{\circ}\cdot 5$, $\theta' = 190^{\circ}$.

T	$3RD(\theta/T)$	$3RE(\theta'/T)$	$3RD(\theta/T) + 3RE(\theta'/T)$	C_p observed.
23	0.395	0.106	0.50	5.25
48	1.85	1.85	3.70	3.42
73	3.31	3.49	6.80	6.38
125	4.77	1.90	6.67	10.52

At higher temperatures, however, the observed values of C_p are higher than the calculated values of C_p . This is probably due to the fact that $C_p - C_v$ has appreciable values at these temperatures.

It is quite evident from the example of NH_4Cl discussed above that when the frequency of lattice oscillation is known, the contribution of the corresponding Debye function is less than the observed value of C_p , if the angular oscillations postulated by Pauling are also present. The heat capacities of a few other crystals with which new Raman lines have been observed in the low frequency region can be examined now from the point of view mentioned above.

CARBON DIOXIDE

It has been observed recently by the present authors¹⁰ that a new Raman line with $\Delta\nu$ equal to 58 cm^{-1} appears in the Raman spectrum of solid carbon

dioxide at about -80°C . It was also pointed out that as the Raman lines due to lattice oscillation involving translational motions of the molecules are forbidden in this case according to selection rules, the new line is not due to a lattice oscillation but may be due to an intermolecular oscillation in groups of molecules, there being weak electronic binding between different molecules in each group. As in this case the heat capacities at low temperatures are known, it can be easily ascertained whether the values of C_p at low temperatures are given by a Debye function corresponding to the observed frequency mentioned above. Since it has been observed in the case of a few organic crystals that the values of $\Delta\nu$ of the new Raman lines in the low frequency region increase by 5 to 10% on cooling the crystal from room temperature up to about -180°C , it may be assumed that the value of $\Delta\nu$ of the new line of solid carbon dioxide increases to about 63 cm^{-1} at low temperatures. Then $\theta = h\nu/k = 90^{\circ}\cdot 3$. Also θ has the same value for all the three degrees of freedom, because the crystal belongs to the cubic system. The calculated values of $3\text{RD}(\theta/T)$ for the three degrees of freedom are given in column 2 of table II. It can be seen that these values are much larger than the observed values¹¹ of C_p given in the last column. Hence the new Raman line

TABLE II.

CARBON DIOXIDE.

(1) T	(2) $3\text{RD}(\theta/T)$ ($\theta = 90^{\circ}\cdot 3$)	(3) $3\text{RD}(\theta'/T)$ ($\theta' = 90^{\circ}\cdot 3$)	(4) $3\text{RD}(\theta''/T)$ ($\theta'' = 90^{\circ}\cdot 3$)	(5) $3\text{RD}(\theta'/T)$ ($\theta' = 150^{\circ}$)	(6) $3\text{RD}(\theta''/T)$ ($\theta'' = 200^{\circ}$)	(7) C_p Calc. ; Col(4) + Col(5) + Col(6)	(8) C_p obs.
15.5	1.69	.40	.10	.50	.00	.60	.61
19.1	2.14	.80	.20	.87	.01	1.08	1.08
25.6	3.13	1.52	.38	1.60	.10	2.14	2.27
36.0	4.45	2.40	.60	2.85	.47	3.62	4.06
47.6	5.91	3.90	.74	3.80	1.08	5.62	5.79
56.2	5.20	3.24	.81	4.28	1.40	6.58	6.77
61.3	5.34	3.32	.83	4.50	1.75	7.08	7.30
81.9	5.61	3.60	.90	5.07	2.47	8.44	8.70
97.9	5.71	3.62	.92	5.32	2.83	9.07	9.42

cannot be due to a lattice oscillation either translational or flexural, the latter involving translational as well as angular oscillation of the molecules about equilibrium orientation as postulated by Venkateswaran. Again, if the new line were due to the angular oscillations of the individual molecules about equilibrium orientation, its contribution to C_v would be $2\text{ R E}(\theta/T)$, because there are two

degrees of freedom for rotation about two axes perpendicular to the axis of the molecule. The values of $\frac{1}{2} R E(\theta/T)$ are given in column 3 of table II. It can be seen that the contributions of another Debye function with three degrees of freedom, which are to be added to the above values of $\frac{1}{2} R E(\theta/T)$ in order to get the values of C_v , become very small, and this is absurd. Hence the new line cannot be due to the angular oscillations. There is another reason for coming to this conclusion. It has been pointed out by Pauling that the amplitude of the angular oscillation diminishes with lowering of temperature and as the intensity of the corresponding Raman line depends on the amplitude, the intensity ought to diminish at low temperatures, if the line be due to angular oscillations. This remark is true also for the flexural oscillation postulated by Venkateswaran. Though the Raman spectrum of solid carbon dioxide has not been studied at temperatures lower than -80°C , it has been observed in the case of benzene, diphenyl ether, *p*-dichlorobenzene and *p*-dibromobenzene that there is no diminution in the intensity of the new lines with the lowering of temperature. Hence in those cases the new lines are not due to angular oscillations of the molecules, and the same may be true also in the case of carbon dioxide.

On the other hand, the contributions of $\frac{R}{2} E(\theta/T) + 2 R E(\theta''/T)$ together with that of $3 R D(\theta'/T)$ with $\theta' = 150^\circ$ and θ'' equal to 200° agree fairly well with the observed values of C_p at the low temperatures. It is difficult to interpret this result but it may mean that as the new line contributes only $\frac{R}{2} E(\theta/T)$ to C_v , it may be due to an ordinary oscillation with one degree of freedom resembling an intramolecular oscillation in a diatomic molecule, because in that case each carbon dioxide molecule as a whole would play the part of an atom and the contribution to C_v per mole, would be $\frac{R}{2} E(\theta/T)$ for the particular oscillation. It is also indicated by the above results that the frequency of lattice oscillation in the case of solid carbon dioxide is much larger than 58 cm^{-1} . It can be seen from table II that the calculated values of C_v are slightly less than the observed values of C_p at higher temperatures. This is probably due to the fact that $C_p - C_v$ may have appreciable values at these temperatures, because $C_p - C_v$ may be roughly equal to $0.0214 \cdot \frac{T}{T_m} \cdot C_p^2$, T_m being the melting point.

SULPHUR

Sulphur is known to exist as S_8 molecules even in solutions and the Raman lines 150 , 216 , 434 and 470 cm^{-1} are observed.¹² The orthorhombic crystals of sulphur, however, give a few more Raman lines besides the above lines. The

lines observed by Venkateswaran¹⁵ are 85, 103, 151, 183, 218, 245, 432 and 472 cm^{-1} . Of these the line 103 cm^{-1} was not observed by Krishnamurti, but since this frequency as well as another less than 77 cm^{-1} are observed in the infra-red, their contributions are also to be taken into consideration while calculating the heat capacities of sulphur. The line 85 cm^{-1} was supposed to be due to the vibration of S_{16} molecule by Krishnamurti and this view was also held by the present authors¹⁷ who observed that this line remains in the same position even at the temperature of liquid oxygen. Venkateswaran has pointed out on the other hand, that this line is due to a lattice oscillation. The correctness of this latter hypothesis can be tested by examining the observed heat capacities of sulphur at low temperatures. If for simplicity we assume that the lattice oscillation has the same frequency 81 cm^{-1} for all the three degrees of freedom, the heat capacities ought to indicate the presence of the contribution of a Debye function, $3 R D (\theta/T)$ with three degrees of freedom and with θ equal to 120° . The calculated values of $3 R D (\theta/T)$ are given in column 2 of table III and the observed values of C_p per gram-atom¹⁶ per degree are given in column 3.

TABLE III.

SULPHUR.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
T	$3RD \left(\frac{\theta}{T} \right)$ ($\theta = 120^\circ$)	C_p obs. per gm-atom per degree	C_p obs. per mole per degree	$3RD \left(\frac{\theta'}{T} \right)$ $\theta' = 47^\circ$	$R \sum_1^3 E \left(\frac{\theta_n}{T} \right)$	$3RD \left(\frac{\theta'}{T} \right) + 4 R \sum_1^3 E \left(\frac{\theta_n}{T} \right)$	(7) - C_p obs.
10	0.207	0.31	2.38	2.42	0.01	2.43	0.05
20	1.582	0.72	5.71	4.59	0.60	5.19	0.55
30	2.906	1.15	9.18	5.30	1.88	7.18	2.0
40	3.948	1.46	11.67	5.54	3.38	8.92	2.75
50	4.51	1.77	14.16	5.69	4.62	10.31	3.85
60	4.92	2.07	16.60	5.78	5.78	11.56	5.04
70	5.18	2.37	18.91	5.84	6.70	12.54	6.4

It can be easily seen that the observed values of C_p do not follow a Debye curve at all. Hence the line 81 cm^{-1} cannot be due to lattice oscillation, because the calculated value of $3 R D (\theta/T)$ with θ equal to 120° coincides with C_p observed at 10°K , but the calculated values are many times larger than the observed values at higher temperatures. Next, let us deal with S_8 molecules and compare

the calculated values with observed values of C_p for the S_8 molecule. The observed values are given in column 4. The contribution to C_p of any Einstein function with θ greater than 40° is very small at 10° K, and therefore the value of C_p observed at this temperature determines the Debye function which is actually responsible for almost the whole of C_p . It can be seen from column 5 that a Debye function with three degrees of freedom and with θ equal to 47° is responsible for the values of C_p for S_8 at the low temperatures. The contribution of any intramolecular oscillation of frequency ν_n to C_p is $R\{E(\theta_n/T)\}$ where the Einstein function has one degree of freedom. The values of $R\{E(\theta_n/T)\}$ are given in column 6. Only six frequencies have been considered so that $\theta_1, \theta_2, \theta_3, \theta_4, \theta_5$ and θ_6 are respectively equal to $100^\circ, 120^\circ, 147^\circ, 220^\circ, 265^\circ$, and 303° . The values of $3RD(\theta'/T) + R\{E(\theta_n/T)\}$ are given in column 7. It can be seen from column 8 that the balances $C_p - \{3RD(\theta'/T) + R\{E(\theta_n/T)\}$ follow an Einstein curve. Hence these are contributions of some other Einstein functions corresponding to some intramolecular oscillations which have not been recorded either in the infra-red or in the Raman spectra.

Thus it is evident that the line 84 cm^{-1} behaves as an intramolecular oscillation. Actually, however, it is not due to an oscillation in a S_8 molecule, because the line is absent in the case of solutions containing S_8 molecules. The above difficulty may be overcome by assuming that pairs of S_8 molecules are present in the crystals so that two molecules in each pair are bound to each other only by a weak electronic binding and that the line 84 cm^{-1} is due to the oscillation of the two S_8 molecules against each other. In order to calculate the value of C_p , however, it is enough to consider the S_8 molecule, and to take into consideration only half the contribution of the corresponding θ_n . If that would be done, the balances in the last column would be larger, but would still follow an Einstein curve. If the frequency of the lattice oscillations were known more definitely, it could be decided whether the molecule is S_8 or S_{16} in the solid state, but the above discussions lead to the definite conclusion that the observed heat capacities of sulphur at low temperatures cannot be explained by assuming the line 84 cm^{-1} to be due to a lattice oscillation.

BENZENE

In the case of solid benzene just below the melting point, two new Raman lines at 63 cm^{-1} and 108 cm^{-1} were observed by Gross and Vuks¹⁷ and at the temperature of liquid oxygen three lines at 81 cm^{-1} , 98 cm^{-1} and 124 cm^{-1} were observed by one of the present authors.¹⁸ The lines are observed to be sharp at the lower temperature and their intensities do not diminish at the lower temperature. The crystals of benzene belong to the space group V_h^{15} with four molecules per unit cell,¹⁹ the molecule itself being centrosymmetrical. If the centres of the four molecules be at $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$, each of these points also becomes

centre of symmetry of the distribution of matter around it. Hence according to selection rules mentioned in previous sections the Raman lines due to vibration of the lattice through one set of molecules against that through any other set are forbidden in this case. It can be therefore assumed that these new lines are not due to lattice oscillation in this case. Also, since the intensity of the lines does not diminish even at -180°C these lines cannot be due either to angular oscillation postulated by Pauling or to the flexural oscillation suggested by Venkateswaran and referred to in the previous sections. If the lines were due to lattice oscillation, their contribution to C_v would be $R \sum_1^3 D(\theta_n/T)$ where $\theta_1 = 116.1^{\circ}$, $\theta_2 = 140^{\circ}.5$ and $\theta_3 = 177^{\circ}.7$. These values are given in column 2 of table IV. It can be seen by comparing these values with the observed values²⁰ of C_p , that the calculated values are much less than the observed values. If the corresponding Einstein functions are calculated, the values of C_v given in column 3 are obtained. These values together with the contribution of a Debye function with θ' equal to $121^{\circ}.5$ and with three degrees of freedom agree with the observed values of C_p up to about 70°K and at higher temperatures the observed values become larger than the calculated values. Since at temperature higher than 90°K , the values of C_p exceed 12 cal./mole/degree, it is evident that besides the above Einstein and Debye functions other Einstein functions are also contri-

TABLE IV.

Benzene.

τ	$R \sum_1^3 D \left(\frac{\theta_n}{T} \right)$	$R \sum_1^3 E \frac{\theta_n}{T}$	$3RD \left(\frac{\theta'}{T} \right)$	C_v Calc. (col. 3 + col 4)	C_p obs.
4	0.009	0.00	0.017	0.017	0.0195
8	0.004	0.00	0.132	0.132	0.147
10	0.159	0.003	0.26	0.263	0.346
20	1.14	0.31	1.54	1.85	1.84
30	2.39	1.25	2.95	4.20	4.24
40	3.37	2.28	3.91	6.10	6.47
50	4.06	3.12	4.51	7.63	8.14
60	4.52	3.74	4.99	8.63	9.32
70	4.85	4.21	5.14	9.35	10.16

buting to C_p at these temperatures. Recently, Lord, Ahlberg and Andrews²¹ have discussed the heat capacities of benzene at low temperatures but they

have not taken into consideration the frequencies of the new Raman lines observed in the low frequency region. On the other hand, they have, assumed that the heat capacities at low temperatures are given by $6RD(\theta/T)$ with θ equal to 150° , where $3RD(\theta/T)$ is for the contribution of translational oscillations of the lattice and the remaining half for that of the oscillation involving a definite phase relation among the angular oscillations of different molecules. They have thus assumed that practically there are two Debye functions instead of one, effective at low temperatures. It has already been concluded from the considerations of the observed intensity of the new Raman lines that the new lines may not be due to any of the two lattice oscillations mentioned above. Therefore the Einstein functions corresponding to these lines are to be taken into consideration. Table IV shows that there is agreement between observed and calculated heat capacities between 4° K and 70° K taking those Einstein functions and one Debye function with $\theta' = 121^\circ.5$. Now it can be seen from table V that at higher temperatures also, there is agreement between observed and calculated values of C_p if the values of $C_p - C_v$ and the contributions $R \sum E(\theta_n/T)$ of internal frequencies of the benzene molecule are taken into consideration. Contribution of the latter Einstein functions as well as the values of $C_p - C_v$ have been calculated by the authors mentioned above and these have been used here. The calculated and observed values are given in table V. Results only up to 130° K have been given because it is evident that if there be agreement between the

TABLE V.

Benzene.

T	$R \sum \frac{3}{1} E\left(\frac{\theta_n}{T}\right)$	$3RD\left(\frac{\theta'}{T}\right)$ $\theta' = 121.5$	$R \sum E\left(\frac{\theta'_n}{T}\right)$	$C_p - C_v$	C_p Calc.	C_p obs.
80	4.55	5.32	0.17	0.54	10.58	10.15
90	4.81	5.44	0.31	0.67	11.23	11.44
100	4.99	5.54	0.51	0.81	11.85	11.99
110	5.15	5.61	0.79	0.97	12.52	12.59
120	5.25	5.66	1.09	1.13	13.13	13.24
130	5.37	5.70	1.45	1.33	13.85	13.96

observed and calculated values up to this temperature, at higher temperatures also there will be agreement.

Thus it is evident that the heat capacities of benzene at low temperatures can be explained without assuming the new lines to be due to lattice oscillations, and in view of the fact that selection rules do not allow the lattice oscillations to appear in the Raman effect, it seems that the calculated value of C_p given in column 5 of table IV, are more reliable than those obtained with the assumption that the new lines are due to lattice oscillations.

Since with *p*-dichlorobenzene, naphthalene and *p*-dibromobenzene, new lines with very small values of $\Delta\nu$ are observed, the values of C_p at low temperatures ought to be very high if these lines be due to lattice oscillations. But data for sufficiently low temperatures are not available and therefore the calculation of C_p has not been possible in these cases.

PALIT LABORATORY OF PHYSICS,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

REFERENCES.

- ¹ Pauling, L., *Phys. Rev.*, **36**, 430 (1930).
- ² Gross, R. and Vuks, M., *Nature*, **135**, 122, 431 and 998 (1935).
- ³ Sirkar, S. C., *Ind. J. Phys.*, **10**, 109 (1935); *Ibid*, 189 (1936).
- ⁴ Sirkar, S. C. and Gupta, J., *Ind. J. Phys.*, **10**, 227 (1936); *Ibid*, **10**, 473 (1936); *Ibid*, **11**, 55 (1937); *Ibid*, **12**, 35 (1938).
- ⁵ Sirkar, S. C., *Ind. J. Phys.*, **11**, 343 (1937).
- ⁶ Venkateswaran, C. S., *Curr. Sci.*, **6**, 378 (1938).
- ⁷ Menzies, A. C., and Mills, H. R., *Proc. Roy. Soc. A*, **148**, 407 (1935).
- ⁸ *Loc. cit.*
- ⁹ *International Critical Tables*, **5**, p. 95.
- ¹⁰ Sirkar, S. C., and Gupta, J., *Curr. Sci.*, **6**, 214 (1937).
- ¹¹ *International Critical Tables*, **5**, p. 86; also cf. Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).
- ¹² Krishnamurti, P., *Ind. J. Phys.*, **5**, 105 and 587 (1935).
- ¹³ Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, **4**, 345 (1936).
- ¹⁴ Barnes, R. B., *Phys. Rev.*, **39**, 562 (1932).
- ¹⁵ Sirkar, S. C. and Gupta, J., *Ind. J. Phys.*, **10**, 473 (1936).
- ¹⁶ *International Critical Tables*, **5**, p. 85.
- ¹⁷ *Loc. cit.*
- ¹⁸ Sirkar, S. C., *Ind. J. Phys.*, **10**, 189 (1936).
- ¹⁹ Wyckoff, *The Structure of Crystals*, 1931, p. 385.
- ²⁰ Ahlberg, J. E., Blanchard, E. R. and Lundberg, W. O., *J. Chem. Phys.*, **5**, 539 (1937).
- ²¹ Lord, R. C., Ahlberg, J. E. and Andrews, D. H., *J. Chem. Phys.*, **5**, 649 (1937).

HARD COSMIC RAY SHOWERS *

By W. BOTHE

Heidelberg

Plate III.

In the year 1931 Heidecke observed an increase of number of coincidence of cosmic rays when he put Pb sheets between the counters which were not placed in the same vertical line. He explained these results to be due to scattering of the primary cosmic rays.

Later on Rossi took up this experiment and showed that new secondary cosmic rays in the form of showers are produced by the inter-action of matter with primary cosmic rays. He found also that the maximum number of secondary cosmic rays are produced by 1.56 cm. thickness of Pb and then a gradual absorption follows up to about 10 cm. thickness. The existence of these secondary particles was beautifully shown by Blackett and others in the Wilson chamber photographs. Anderson by the analysis of these shower photographs discovered the positron—a positively charged particle of electronic mass.

Ackemann, Hummel and others observed that by increasing the thickness of Pb, again secondary particles are produced which reaches its maximum at about 17 cm. thickness of Pb. Drigo found that these secondary particles are entirely absorbed by 1 cm. thickness of Pb—a result which seems at first quite surprising. The shower producing rays having range of 17 cm. thickness of Pb produces secondary rays which have only 1 cm. range.

The showers of first kind are groups of positive and negative electrons which approximately proceed from the same point and cover a tolerably large range of angles, on the average 20° about the axis. Their penetrating power is rather low, about 2 cm. of Pb absorbing the shower particles nearly completely. What I intend to report today concerns the showers of second kind which differ from the usual showers not only in the above-mentioned characteristics, but also in the way in which they originate.

You see here (fig. 1) an experimental arrangement, which does not appear to be very different from those which Rossi and many others after him have utilized for the investigation of shower: four Geiger tubes are in coincidence arrangement, the two upper ones being connected in parallel, above that is the shower producing layer in variable thickness; between the upper and

* Lecture delivered at the annual meeting of the Indian Physical Society held at Calcutta, in January, 1938.

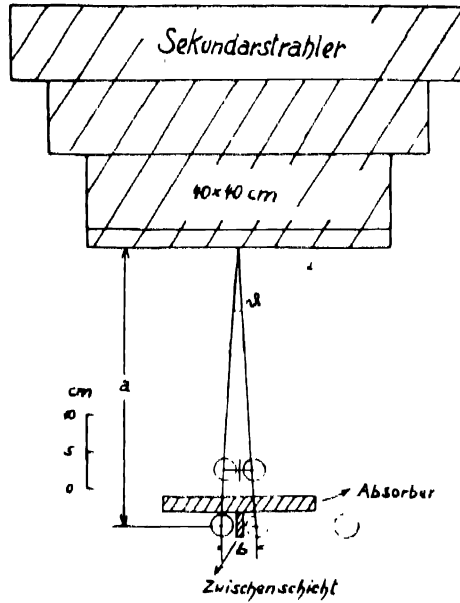


FIGURE 1.

lower pairs of counters an absorber of different thickness may be inserted. By altering the thickness of the shower-producing layer, one can obtain the Rossi-curves. This has a very pronounced maximum at 1.7 cms. of lead. By altering the thickness of the absorber, one obtains the absorption curve of the particles. All the curves which have been obtained so far, show that the usual sort of shower particles are absorbed, for the most part, by

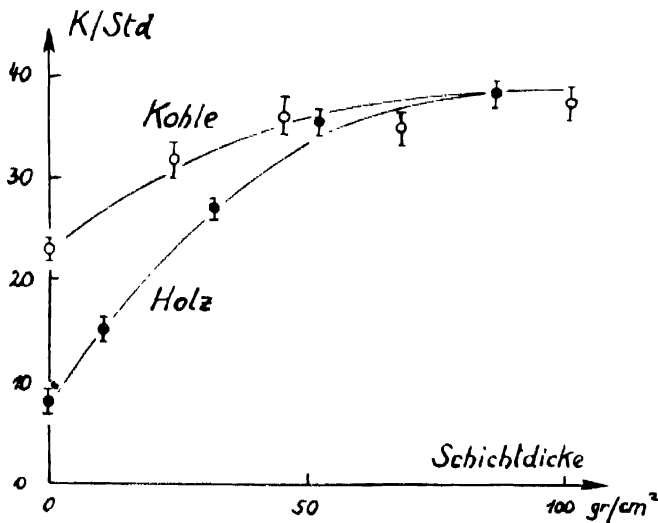


FIGURE 2

2 cms. of lead. Accidentally, with our arrangement, we made a different observation: when we inserted 2 cms. of lead between the counters, we obtained still more than half of the coincidences, which occurred without the absorber. This signifies that a secondary corpuscular radiation comes from the matter above the counters, which is essentially more penetrating than the known shower particles. We also took their Rossi-curve, by altering the thickness of the shower-producing layer.

You see, that up to a thickness of about two hundred grams per cm^2 the curve rises, whereas for lead, for a thickness exceeding 18 gm/cm^2 the curve goes down. This also means that the saturation thickness of our secondary particles is greater than that of the useful showers. What could be the cause of it? Our arrangement differs from the usual in two points: firstly, the shower-producing substance consisted of light atoms (carbon, wood); secondly, the angular distance of the counters, as seen from the layer, was particularly small, therefore coincidences could only be produced by two particles, which subtend only a small angle at each other. It was to be tested, as to which of these two points was essential. We tested first the second point, the dependence of the penetrating power of the secondary particles on the angle of divergence. For this purpose, either the counters had to be brought into greater or smaller distance from each other in horizontal direction, or the whole counter arrangement had to be brought into greater or smaller distance from the shower-producing layer.

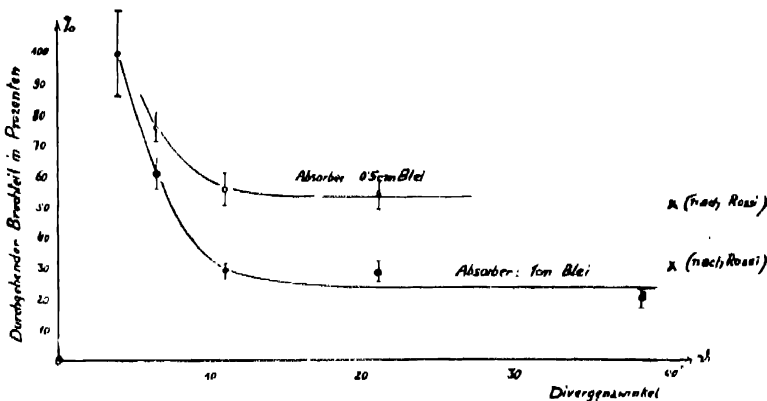


FIGURE 3.

In the next diagram (fig. 3) the abscissa are the angles of divergence, the ordinates are the frequencies of coincidences, relative to the frequency without the absorber. The two curves hold for an absorber, of 0.5 and 1 cm. of lead each. You see, the answer to our question is clear. At large angles you find the well-known penetrating power of the usual shower particles: 1 cm. of lead absorbs

more than half. On the other hand, at small angles the particles are much more penetrating, and at 4° one cm. of lead absorbs only a small part of the shower particles. We conclude there from, that the hard showers occur only at angles smaller than 10° .

You may ask why these showers have never been observed before? It is very remarkable, but it appears that up to this time no one has made observation at so small angles. At the same time, a phenomenon is already known from which it can be inferred that possibly it is connected with our hard showers, that is, the so-called second maximum of the Rossi-curve. If the Rossi-curve be continued till to much larger thickness of the shower-producing layer, then it again begins to rise, and it attains a second maximum at about 17 cms. of lead. This large saturation thickness signifies again a hard secondary radiation. It is true, the existence of this second maximum has been called into question by certain authors. But in every case it could be supposed that here we have also a reaction of the hard showers. This question could be very simply tested: one has to measure the Rossi-curves for different angles of divergence. The result of such measurements is shown in the next figure (fig. 4).

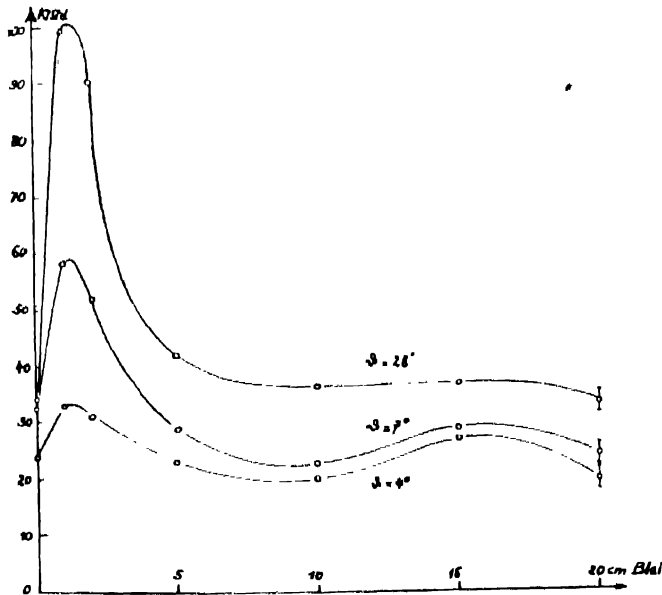


FIGURE 4.

I believe that here the result is also very clear. At an angle of divergence amounting to 28° , the second maximum can scarcely be recognised; at 7° , the second maximum appears quite distinctly, and at 4° , it is almost as high as the first maximum. Now we have seen that in fact the hard showers occur only at angles smaller than 10° , therefore no doubt can remain that the second maximum

Fig. 6 (a)

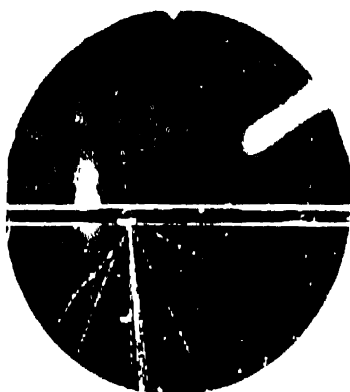


Fig. 6 (b)

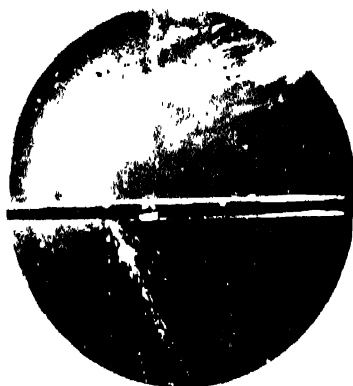
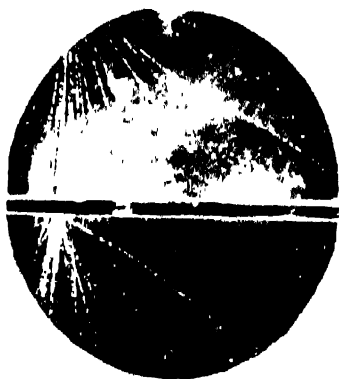


Fig. 6 (c)



Cosmic ray showers.

is produced by the same hard showers as we have observed. At the same time, it becomes clear why the observations made so far were so contradictory. It has not been grasped that the angle is of such importance.

Actually, this question is somewhat more complicated, as I intend to say in brief. We have seen that at angles greater than 10° , the second maximum is very insignificant, but it still exists, the intensity has not diminished to zero. A further difficulty appeared, as we measured more accurately the absorption curves of the shower particles under different conditions. If we observe in the second maximum, and the angle of divergence is large, we get no hard showers, but the usual soft showers. At first, it seems unintelligible that a secondary radiation reaches its saturation in as much as 17 cms. of lead, while it is almost completely absorbed in 2 cms. of lead. I shall now show how these two observations can be reconciled. The particles which are observed in this case are of tertiary origin.

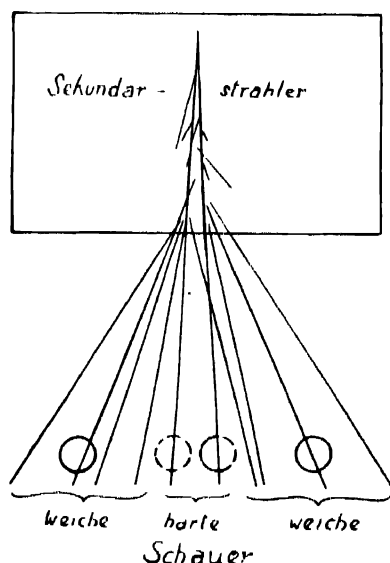


FIGURE 5.

The hard showers themselves are able to produce soft showers, and this process comes forth already in the shower-producing layer itself. These tertiary showers have apparently all the characteristics of the usual soft showers, in particular, they have large angles of divergence. Therefore at large angles, the hard showers cannot directly produce coincidences, but can do so by the circuitous way of the tertiary soft showers.

It is now very interesting that all these deductions find a strong support in some Wilson photographs, which Auger and Ehrenfest have published, after we have made our first communication about the hard showers. In

the next figure (plate III) you see a shower of small angular divergence. We are now convinced that this is the new kind of shower. This shower is surrounded by a usual shower of large divergence. According to our conceptions, the soft shower is produced by the hard one, in the interior of the layer.

Another photograph (fig. 6 c) obtained by Anger and Ehrenfest shows a compound shower coming from above, the hard shower releases out of a layer of lead a tertiary shower; that is exactly the process which we have assumed.

Now I wish to make a few short remarks about the generation of the hard showers. The question arises, how does the intensity of the hard showers depend on the nature of the shower-producing substance.

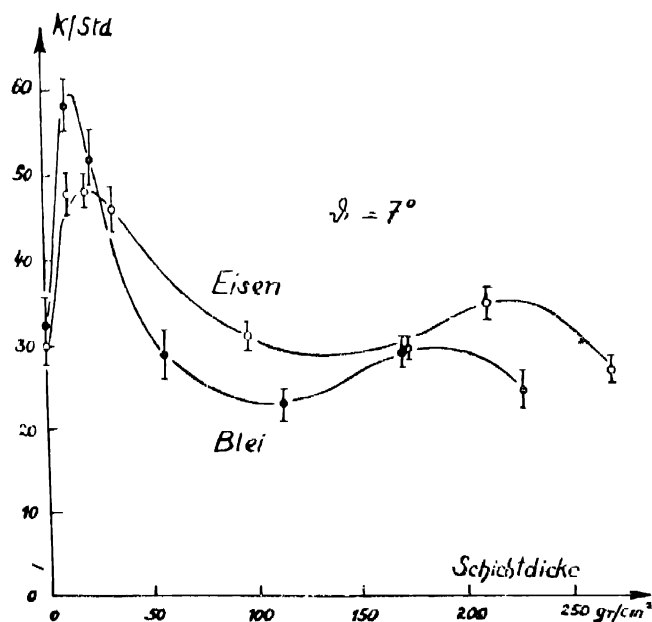


FIGURE 7.

In the next diagram (fig. 7) you see the Rossi-curves for lead and iron, taken under identical conditions. The first maximum is clearly lower for iron than for lead. This is not new, but has been verified by different observers. It has been established that for a small thickness, the intensity is approximately proportional to Z^2 per atom. This result obviously holds for the soft showers which produce the first maximum. But the matter is quite otherwise for the second maximum which is produced by the hard showers. Here the intensity is at least as great for iron as for lead, the intensity therefore appears to be approximately proportional to Z per atom. This may be an important criterion for distinguishing between the two kinds of showers.

Finally, we may ask about the primary radiation which produces the hard showers.

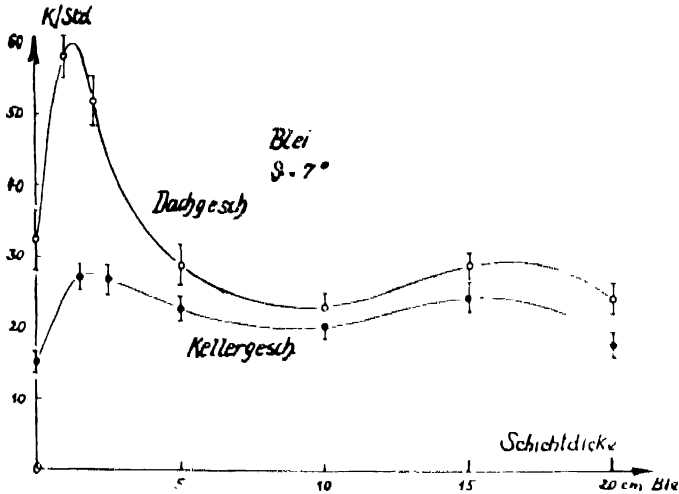


FIG. 8.

In the next diagram (fig. 8) you see the Rossi-curve for lead, obtained under the same conditions, but firstly under the roof of the Institute, then under the basement. The intervening ceilings had about 270 gm/cm^2 , they worked as filter for the shower-producing primary radiation. You see that by filtering the primary radiation, the first maximum is strongly reduced; the second maximum, on the other hand, shows little difference. This shows that the soft showers are produced by the so-called soft component of the primary radiation, as has been known for a long time; the hard showers on the other hand are produced by the hard component of the primary rays. This is again an important criterion for distinguishing between the two kinds of showers.

Here I must not forget to mention that some time ago Rossi has already made similar experiments: they were not so complete, that any definite conclusions could be drawn from them, but Rossi had already suspected that the shower phenomena are of a complex nature

I am afraid that I have busied myself too long with description of the experiments, carried out in the main part by K. Schmeiser. But to my great sorrow, I can give no theory of these phenomena. Perhaps, in this case, the new particles assumed by Anderson, and Street and Johnson play a part

In final, I may say, that after all what we know of the shower phenomena, we must distinguish between at least three kinds of showers: firstly, the soft showers, which, according to Bhabha and Heitler, arise through the mutual conversion of electrons into photons and *vice-versa*; secondly, the hard shower, about the nature of which we know very little, and thirdly, the Heisenberg showers or, explosion showers, which can be conceived as arising out of evaporating nuclei, and which appear to be realised in the stars obtained on photographic plates exposed to cosmic rays, as was demonstrated to you by Prof. Taylor, and which have also been observed by Blau and Wambacher in Vienna.

A STUDY OF SULPHUR ALLOTROPES BY THE X-RAY DIFFRACTION METHOD *

PART I

By S. R. DAS

(Calcutta University)

(Received for publication, April 8, 1938.)

Plates IV and V.

ABSTRACT. The structures of the various modifications of sulphur at temperatures ranging between -183°C and 130°C have been investigated by Hull's diffraction method. The following important observations and conclusions have been made.

1. Ordinary roll sulphur and flower of sulphur have identical crystalline structures similar to that of the orthorhombic sulphur (S_{α}).

2. Milk of sulphur and the gummy deposits of colloidal sulphur which are insoluble in CS_2 and regarded as amorphous, are really crystalline. Their patterns clearly indicate that they are identical in structure with S_{α} .

3. Plastic sulphur when freshly prepared by pouring boiling sulphur in cold water, is really amorphous, producing only one diffuse band ($d \approx 3.5 \text{ \AA}$). It rapidly transforms into a hard solid mass insoluble in CS_2 , which has a structure similar to that of S_{α} . When kept at a high temperature (about 60°C), or treated with strong NH_4OH the substance becomes soluble in CS_2 .

4. White sulphur obtained by the hydrolysis of S_2Cl_2 , hitherto supposed to be amorphous, has exhibited a well-defined crystalline pattern, quite different from that of S_{α} . It is insoluble in CS_2 . When heated for some time at about 88°C , it transforms entirely and permanently into S_{α} .

5. The insolubility of the various forms of sulphur has been suggested to be, some way, due to the presence of SO_2 on the surface of the crystallites.

6. The special features characterising the patterns obtained at temperatures lying between 80°C and 110°C are : (a) the discontinuity of the rings, (b) the appearance of asterism, i. e., radial streaks, and (c) the appearance of a large number of sharp intense spots arranged irregularly on the plate. It has been shown that the changes noticed in the pattern are due to the growth of the crystal size in the heated exposed specimens of powdered sulphur (S_{α}), and have nothing to do with the enantiotropic transformation of S_{α} into S_{β} which is generally known to take place at 95.5°C or above.

7. All attempts in recording a pattern of S_{β} failed probably due to (a) the instability of S_{β} at the ordinary room temperature and (b) the growth of crystal-size and the disfiguration of the patterns at higher temperatures where S_{β} is stable.

* Communicated by the Indian Physical Society.

8. Patterns of liquid sulphur have been obtained at 114°C , 119°C and 128°C , and in each case two bands have been obtained.

9. No appreciable change in the pattern has been observed at as low a temperature as -183°C .

INTRODUCTION

An extensive Physico-Chemical study of sulphur led to the discovery of a large number of its allotropes, both crystalline and amorphous. Though the multifarious complexities of the element have been engaging the time and attention of a large number of investigators who in gradual steps, have explicated some of the multifold peculiarities of sulphur, still there are many interesting but obscure points awaiting plausible explanations and demanding a systematic investigation on the subject. The representation made here describes the results obtained by the present author during the course of a systematic study of the various modifications of sulphur, under different physical conditions by the X-ray method.

A brief outline of our present knowledge of sulphur and its allotropes concerning the subject-matter of the present investigation is stated below.

1. SULPHUR AND ITS ALLOTROPEs

(a) Orthorhombic sulphur¹ (S_a)

Ordinary roll sulphur and almost the whole of the flower of sulphur belong to this class. Sulphur crystallised from a cold solution in CS_2 also forms a orthorhombic system. This variety has been analysed by the X-ray method by Bragg,² Mark and Wigner,³ and Warren and Burwell.⁴ The final result obtained from these analyses indicates a space group V_2^h . The size of the unit cell is found to be, $a = 10.48$, $b = 12.92$ and $c = 24.55$ in Angstrom units. Each cell contains sixteen S_8 molecules or 128 atoms. This variety of crystalline sulphur is stable at the ordinary temperature.

(b) Monoclinic sulphur (S_B)^{5,18}

Several varieties of monoclinic sulphur have been observed and described by the crystallographers but amongst them, the needle shaped crystal obtained from molten sulphur is the most common type. It is very unstable below $95^{\circ}.5\text{ C}$ and is reported to be stable above this temperature. S_a and S_B are known as enantiotropic, the accepted value of the transition temperature corresponding to $S_a \rightleftharpoons S_B$ is $95^{\circ}.5\text{ C}$. Orthorhombic sulphur is stable below and unstable above this temperature. No X-ray analysis of S_B has yet been attempted.

(c) *The amorphous allotropes of sulphur*

These amorphous allotropes of sulphur are obtained only by very special means. The well known varieties are : (i) Milk of sulphur,⁶ (ii) Colloidal sulphur,⁷ (iii) White sulphur,⁸ and (iv) Plastic sulphur.⁹ J. J. Trillat and J. Forestier¹⁰ have analysed this substance after stretching its thread from 8 to 10 times its original length. They have concluded that the substance is crystalline and the axial lengths are different from those of S_8 . Plastic sulphur under ordinary conditions is known as amorphous, but it quickly solidifies into a hard mass consisting of S_8 and S_{μ} . S_8 is soluble in CS_2 and crystalline, while S_{μ} is insoluble in CS_2 and amorphous.⁹

(d) *Liquid sulphur*

The accepted values of the melting points* of pure S_8 and of pure S_{μ} are $113^{\circ}\cdot 0$ C and $119^{\circ}\cdot 4$ C respectively.¹¹ But here also the opinions of the different authors vary widely. The liquid sulphur is supposed to contain two types of sulphur S_{λ} (soluble in CS_2) and S_{μ} (insoluble in CS_2) and the proportion of the latter increases with the temperature. If a quantity of molten sulphur is allowed to solidify, the proportion of soluble and insoluble sulphur in the solid depends on the relative amounts of S_{λ} and S_{μ} present in the liquid at the time of solidification.⁹ The plastic sulphur which is prepared by pouring boiling sulphur into cold water is also sometimes called a super-cooled type of S_{μ} .⁹

Blatchford¹² has studied liquid sulphur at temperatures ranging from 130° C to 210° C by the X-ray diffraction method. From the experimental results he concludes that the sulphur molecules have a more or less regular grouping amongst them and further the spacing corresponding to the diffraction ring does not conform to the close packing theory. At about 180° C he has observed a sudden change in the value of the spacing which is correlated with the well known change of viscosity of the fluid at a neighbouring temperature.

2. EXPERIMENTAL

The powder photograph method is chiefly adopted in the present investigation. The slit system (fig. 1) is of special design. It behaves both as a slit and also as a supporter of the specimen under examination. It consists of a thick-walled brass tube A, $\frac{3}{4}$ " in outer and $\frac{1}{4}$ " in inner diameter, and 8 c.m. in length. The tube is closed at the ends by means of two brass plugs B and C. The plug B on the tube-side of the slit has a bore of 1 m.m. co-axial with the main tube A, while C lying on the plate-side has a bore of 0.4 m.m. In

* The values of the m. pts. of sulphur as recorded by different authors widely vary. For rhombic sulphur it varies between $112^{\circ}\cdot 8$ C (Partington, *A Text Book of Inorganic Chemistry*, 1938, p. 488), and $119^{\circ}\cdot 25$ C (Mellor, *Modern Inorganic Chemistry*, 1919, p. 400).

order to protect the plate from the rays scattered by the slit, a shield-tube D is screwed on to A against C at the plate-end of the slit.

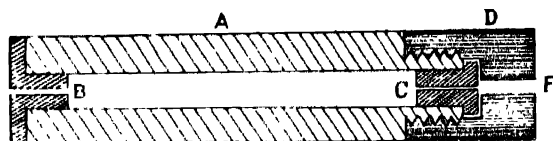


FIGURE 1.

The cell containing the diffracting material of proper thickness was placed in direct contact with the face of the shield D at F by means of a washer and a couple of screws. The shield D, along with the cell is easily demountable and serves another important purpose, *i.e.*, during the exposure on the same plate, the cell can easily be re-filled by the diffracting material at any desired interval of time. This device is of great assistance when one has to examine by X-ray diffraction, some volatile substance, or an unstable substance which is liable to change its modification under the experimental conditions specially when the rate of transformation is very rapid. It is convenient in such cases to have two exactly similar detachable shields, so that one of them may be kept ready in hands with the refilled cell immediately before the first cell is required to be withdrawn. The second cell is then put before the slit system, thus saving considerable amount of time.

For investigating the material kept at a high temperature during the exposure, an electric heater was employed, where any particular temperature measured by a thermocouple, could easily be maintained within 2° C, by sliding resistances. A cylindrical Cyndanio hobbin coiled with nichrome wire formed the simple heater, and the axial bore of the hobbin exactly fitted the slit tube.

The experiments with sulphur S_8 at lower temperatures were conducted with carbon dioxide snow, liquid oxygen, etc., and a special vacuum chamber was constructed for this purpose; but the present paper records only results of preliminary experiments, so far as the low temperature works are concerned and a full description of the apparatus is deferred at the present moment. The various forms of sulphur used in the present investigation were prepared by the author in this laboratory. The chemicals used for the purpose were either the preparations of E. Merck or of Schering Kahlbaum.

3. RESULTS

A. Orthorhombic sulphur (Fig. 4) *

Fine powders of roll sulphur, flower of sulphur and sulphur recrystallised

* The distance between the cell and the photographic plate is different for different photographs. For figures 2, 3 and 4 the distance R is 2.452 c. m. for figures 5, 6, 7, 10, 13 and 14, R is 1.965 c. m. for figures 8, 9 and 12, R is 2.248 c. m.; for figure 11, R is 2.370 c. m. In the final print, the figures are reduced to three-fourth of the original size.

Fig. 2.

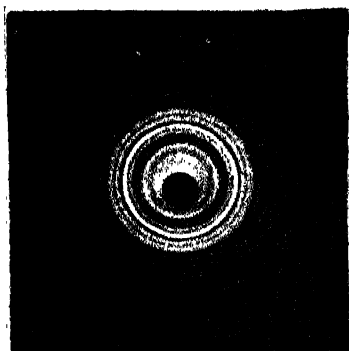


Fig. 3.

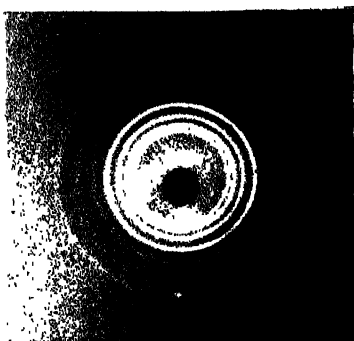


Fig. 4.

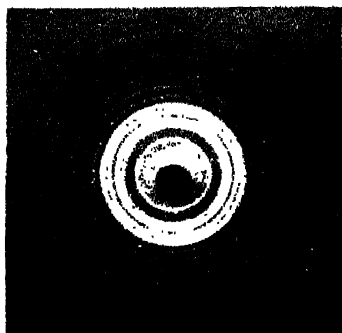


Fig. 5.

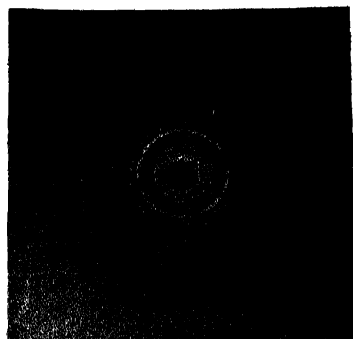


Fig. 6.

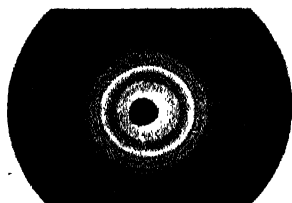
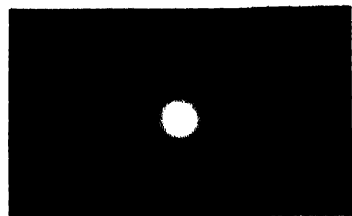


Fig. 7.



Powder diagrams.

Fig. 2 — White sulphur after heating at 88° C.

Fig. 3. — White sulphur.

Fig. 4 — Recrystallised sulphur.

Fig. 5. — Hardened plastic sulphur rendered soluble by NH_4OH .

Fig. 6. — Hardened insoluble plastic sulphur.

Fig. 7. — Colloidal deposit of sulphur.

from a solution in CS_2 were examined. These forms of sulphur are known to belong to the rhombic type of crystals. The diffraction patterns obtained in these cases also support this view. For, the values of the Bragg-spacings and the intensities of the corresponding rings in the patterns of the different members closely agree with one another.

B. Milk of sulphur (Fig. 14)

This is one of the well known varieties supposed to be amorphous. To a freshly prepared solution of calcium polysulphide, dilute acid (1 acid : 1 water) was gradually added, when a milky white precipitate with slightly yellowish tinge was obtained. Two different samples of this variety were prepared by acidulating with (a) dil. HNO_3 and (b) dil. HCl . These varieties are found to exist in a state of extremely fine division and were exposed to X-ray without any artificial powdering. The ring systems of the two samples are similar to each other and also to that of orthorhombic sulphur S_8 . The sharpness and the continuity of the rings produced by milk of sulphur clearly indicate that the sizes of these minute crystals lie between 10^{-3} to 10^{-5} c.m. in each direction. Thus we find that milk of sulphur is not really amorphous, but is crystalline and the structure is exactly similar to that of the orthorhombic α -sulphur. During the precipitation of milk of sulphur, the colour of the precipitate appeared perfectly milk-white immediately after its formation, but very soon turned slightly yellowish. This was evidently due to the conglomeration of white smaller particles into bigger ones which are generally yellow.

C. Colloidal sulphur

This modification of sulphur was prepared in the state of colloidal suspension in water, by passing pure H_2S through a concentrated solution of SO_2 in water at about 5°C – 10°C . The colloidal solution obtained in this way was filtered twice and preserved. Deposition of gummy solid sulphur took place from this solution spontaneously but the rate was extremely slow. The colour of a concentrated solution of colloidal sulphur appears yellow by reflected light, but deep reddish brown by transmitted light. The yellow colour gradually gets fainter and finally disappears with the increase of dilution; but at a certain stage, the reflected colour becomes bluish, while the colour of transmission still remains brown. To a quantity of the colloidal solution, we added a strong solution of NH_4OH * which coagulates the colloidal particles, and the deposits

* It is a well-known fact that a suitable electrolyte may deposit particles held in colloidal suspension. The special reason for selecting NH_4OH in the present case was that it could be driven out of the deposit by simple evaporation.

formed by spontaneous sedimentation and by the addition of NH_4OH were analysed by X-rays.

The diffraction rings obtained in the cases of these two types of colloidal deposits of sulphur are exactly similar to those of S_α . The rings are quite sharp but are slightly broader than the corresponding rings of orthorhombic sulphur. This fact naturally suggests that the particles in colloidal deposits are very small so that sufficient number of lattice planes are not available for the production of sharp rings.^{13,14} Similar observations have been made by many observers in the cases of colloidal particles of metals,^{15,16} which on analysis have exhibited their crystalline structures. Colloidal particles of sulphur are therefore not amorphous but consist of extremely minute crystals of the orthorhombic type (S_α).

We made an attempt to obtain the diffraction patterns of the colloidal sulphur particles in their state of suspension in water. But so far no ring system of sulphur was observed. Only a wide band due to water appeared in the photographs.*

D. Plastic sulphur (Fig. 13)

This is the widely known amorphous allotrope of sulphur.⁹ We prepared it by pouring boiling sulphur into cold water in thin streams. A highly sticky deep-brown (almost black) substance was obtained. A small quantity of this substance was laid in a thin layer on a piece of very thin paper by means of a clean glass rod. The film was then applied on the carrier as described in previous sections.

Plastic sulphur is known to be highly unstable under ordinary laboratory conditions. For this reason in the present investigation the specimen of plastic sulphur was replaced at an interval of one hour during the exposure. Several photographs were taken in this way and the pattern obtained in each case consisted of a single diffuse band corresponding to the Bragg spacing 3.5 Å. In one case we allowed the one and the same specimen to be exposed for about 4 hrs. and the photograph obtained consisted of several faint but sharp rings like those of S_α . This, therefore shows that plastic sulphur had considerably transformed into S_α within four hours. Plastic sulphur as it is produced is really amorphous and the present work shows that it is the only amorphous form of sulphur. J. J. Trillat and J. Forestier¹⁰ have analysed a thread of plastic sulphur after extending it, by longitudinal tension, from 8 to 10 times its original length. The photograph revealed a fibre-pattern. From this they have come to the conclusion that the substance is crystalline. The identity period in the direction

* Recently with improved technique, the ring systems of sulphur particles suspended in water has been studied.

Fig. 8.



Fig. 9.

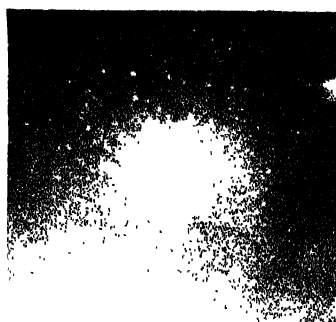


Fig. 10.

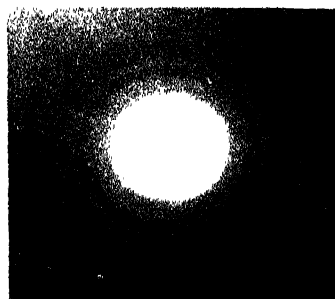


Fig. 11.

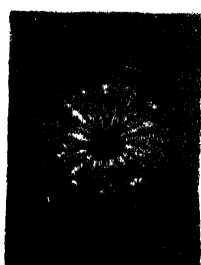


Fig. 12.

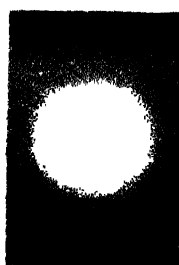


Fig. 13.

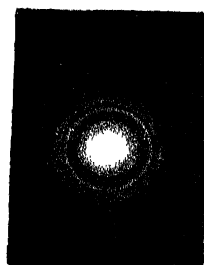


Fig. 14.

Powder diagrams.

Fig. 8.—Sulphur heated at 104°C for 40 hours.

Fig. 9.—Sulphur heated at 104°C for 60 hours.

Fig. 10.—Sulphur in collodion at 104°C .

Fig. 11.—Liquid sulphur at 117°C .

Fig. 12.—Sulphur heated at 104°C for 10 hours.

Fig. 13.—Fresh plastic sulphur.

Fig. 14.—Milk of sulphur.

of the fibre is found to be equal to $9.35 \text{ \AA}$ which approximates to the length of the a -axis ($10.61 \text{ \AA}$) of S_a . This observation admits of two explanations: (1) As plastic sulphur is extremely unstable it is mostly converted during the time of exposure (6 hrs.) into the orthorhombic crystallites which, under the force of tension, oriented with their a -axis more or less parallel to the applied force. This certainly can not adequately account for the considerable shortening (about 12.5%) of the a -axis of fibrous plastic sulphur. (2) Another explanation to which we may direct our attention, depends upon a possible similarity between a thread of plastic sulphur and a piece of rubber. The latter though amorphous under ordinary conditions, produces a fibre pattern, when extended by tension and the sharpness of the pattern increases with the degree of extension.^{21, 25} This behaviour of rubber is satisfactorily explained by the supposition of the preferred orientation of the highly polymerised isoprene (C_5H_8) molecules present in it. In the case of plastic sulphur we may well assume that the S_8 molecules or any higher complex present in it may behave exactly in the same way as the molecules of rubber. But a clear unambiguous explanation requires further investigations.

II. Hardened plastic sulphur (Fig. 6).

It has been mentioned that plastic sulphur solidifies into a very hard and brittle grey mass when kept for a few hours at ordinary temperatures.⁹ We have observed that the transformation into the solid state is accelerated by the elevation of temperature ($70^\circ\text{C} - 100^\circ\text{C}$), but the solid in the latter case does not become so hard. It becomes, rather friable and falls to powder even by the pressure of the fingers. There is another difference in the two types of solidified plastic sulphur, the hard variety (formed at the room temperature) is almost entirely insoluble whereas the second variety (formed at $70^\circ\text{C} - 100^\circ\text{C}$ or above) is completely soluble in CS_2 . Both the soluble and the insoluble specimens produce exactly similar patterns, the inner rings of the insoluble specimen are slightly diffuse (Fig. 6).

The coarsely powdered insoluble variety as well as the thin film of hardened plastic sulphur produced identical patterns, resembling those of the thoroughly powdered specimen. This also shows that the crystal grains in the insoluble specimens are extremely small. But the specimen soluble in CS_2 behaved in a quite different manner. The diffraction rings in this case ceased to be uniform when the powder was coarse, indicating that heat had caused a growth of the micro-crystals. We have observed a similar phenomenon of growth at higher temperature in the case of ordinary sulphur, which will be described in a later section.

F. *Hardened plastic sulphur rendered soluble by NH_4OH (Fig. 5)*

A quantity of the hard insoluble mass was thoroughly powdered and kept in a stoppered bottle containing a strong solution of ammonia. After three days we examined the powder which was first thoroughly washed and desiccated. It became almost completely soluble in CS_2 and the diffraction pattern obtained in this case was free from the diffuseness which was observed in the case of the untreated specimen. The powders required no further powdering for the production of continuous rings, indicating that no growth of the crystal size had taken place. This observation is of much importance inasmuch as it helps us to understand the exact nature of the plastic sulphur. The observed diffuseness of the rings of the insoluble specimen was first assumed to be due to the joint actions of the probable distortion of the crystal lattice formed by sudden cooling and to the extreme smallness of their sizes. This idea was further strengthened by the fact that the insoluble specimen when heated not only shows clear signs of crystal growth but also gives rise to a system of sharp rings under proper conditions.

This idea had to be modified. For, we can conceive of no mechanism by which NH_4OH can bring about a growth of the crystal size. Therefore, the diffuseness of the rings produced by insoluble solidified plastic sulphur must be due to some other factor.*

G. *Solubility and insolubility of sulphur*

Table (I) briefly summarizes our knowledge about the point. From a study of the table we can generalise that whenever an insoluble variety of sulphur is produced, SO_2 is always present in the reactions involved. This naturally suggests that insolubility may be due to the presence of SO_2 which forming a shielding layer on the surface of the small crystal grains prevents them from coming in contact with the solvent. This idea is further corroborated by solubility of solidified plastic sulphur which has been treated with NH_4OH or has been heated to a high temperature. The latter possibly drives out and the former chemically reacts with the SO_2 gas and thus in both the cases the sulphur grains are rendered free from the SO_2 layer and the solubility is restored.

* Recently the problem of solubility or insolubility of the various types of sulphur has been carefully studied and the results will be published later.

TABLE I.

The solubility or insolubility of the different types of sulphur in carbon disulphide.

	The variety of sulphur.	Structure.	Nature	Chemical reactions in preparations.	
1	Roll sulphur	...	S_{α}	soluble	
2	Flower of sulphur (Merck)	.	S_{α}	soluble	
3	Milk of sulphur	...	S_{α}	soluble	$\text{CaS}_x + 2\text{HCl} = \text{CaCl}_2 + x\text{S}$.
4	Colloidal sulphur	...	S_{α}	insoluble	$3\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O}$.
5	White sulphur	...	S_{ω}	insoluble	$\text{S}_2\text{Cl}_2 + 2\text{H}_2\text{O} = 3\text{S} + \text{SO}_2 + 4\text{HCl}$.
6	White sulphur heated to 88°C	...	S_{α}	soluble (partly)	
7	Fresh plastic sulphur	...	amorphous	insoluble	Boiling S suddenly poured in cold water. (S burns in air to SO_2 .)
8	Hardened plastic sulphur	.	S_{α}	insoluble	
9	Hardened plastic sulphur heated to a high temperature, or treated with a strong solution of NH_4OH .		S_{α}	soluble	
10	Monoclinic sulphur	...	S_{β}	soluble	

The following table II shows the Bragg-spacings of (a) roll sulphur, (b) flower of sulphur, (c) recrystallised sulphur, (d) milk of sulphur, (e) colloidal sulphur and (f) insoluble hardened plastic sulphur. The lattice planes producing the rings have been identified by using Warren and Burwell's ⁴ values of the dimensions of the unit cell of orthorhombic sulphur. The Millerian indices of these planes are given in the ninth column.

TABLE II.

Obs. spacings $\times 10^3$.	Intensity.	Roll sulphur.	Flower of sulphur	Recrystallised sulphur.	Milk of sulphur.	Colloidal sulphur.	Hardened plastic S.	Indices of the planes.	Calc. spacings $\times 10^3$.
d_1	m.s.	5.66	5.66	5.66	5.66	5.66	5.66	022	5.71
d_2	v.s.	3.84	3.85	3.84	3.84	3.84	3.84	222	3.84
d_3	s.	3.45	3.45	3.45	3.45	3.45	3.45	020	3.45
d_4	s.	3.14	3.14	3.14	3.15	3.14	3.14	210	3.13
d_5	m.s.	2.85	2.84	2.84	2.86	2.83	2.82	044	2.85
d_6	w.	2.64	2.64	2.64	2.63		2.63	400	2.65
d_7	v.w.	2.41	2.40	2.41			2.41	404	2.41
d_8	w.	2.25	2.24	2.26					
d_9	v.w.	2.12	2.12	2.12	2.12		2.11	062	2.12
d_{10}	v.w.	1.98	1.98	1.98			1.99	441	1.99
d_{11}	v.v.w.			1.91			1.90	264	1.89
d_{12}	v.v.w.		1.80	1.79					
d_{13}	v.v.w.			1.74				602	1.74

H. *White sulphur*⁸

The study of white sulphur which had hitherto been regarded as amorphous was very interesting and it led to quite unexpected results.

A quantity of redistilled sulphur monochloride (S_2Cl_2) prepared by passing perfectly dry chlorine over molten sulphur,¹⁷ was hydrolysed by the addition of a sufficient quantity of distilled water. At first a sticky mass was formed which subsequently turned into a hard greyish solid substance known as white sulphur.

A thoroughly powdered specimen was examined by X-rays. The nature of the diffraction pattern (Fig. 3) showed clearly that white sulphur consisted of minute crystals, the perfection of which is in no way inferior to that of carefully recrystallised S_8 from a solution in CS_2 . In order to form an idea about the size of the crystals in white sulphur, a very thin film of white sulphur was prepared. During the hydrolysis of S_2Cl_2 , when a gummy soft mass was formed at a certain stage, a small quantity of it was pressed between two photographic glass plates to sufficient thinness. The soft film so obtained was subsequently treated with water until the hydrolysis was complete. This film was exposed to X-rays and the diffraction pattern bore a point-to-point resemblance to that of the powdered specimen. It thus became evident that the crystals as they grew during the process of hydrolysis were extremely small, so that a complete random orientation of the lattice-planes relative to the X-ray beam was possible. The simultaneous presence of sharpness and uniform intensity in the diffraction rings clearly shows that the extension of the crystal grains in each direction lay within the range 10^{-3} to 10^{-5} c.m.¹³

TABLE III.

Spacing $\times 10^8$.	Intensity.	White sulphur	Spacing $\times 10^8$.	Intensity.	White S. after heating.	Intensity.	Recrystallised sulphur.
d_1	m.s.	4.50	d_1	m.s.	5.66	m.s.	5.66
d_2	s.	4.02	d_2	v.s.	3.85	v.s.	3.84
d_3	s.	3.56	d_3	s.	3.45	s.	3.45
d_4	s.	3.07	d_4	s.	3.09	s.	3.14
d_5	v.w.	2.71	d_5	m.s.	2.84	m.s.	2.84
d_6	v.w.	2.30	d_6	w.	2.64	w.	2.64
d_7	w.	2.10	d_7	v.w.	2.11	v.w.	2.12

Measurements of diffraction rings of white sulphur revealed that the crystals of white sulphur have a structure quite different from that of S_α . The table (III) shows the values of the Bragg-spacings of white sulphur and their relative intensities on an arbitrary scale.

White sulphur or S_ω^* is a highly stable crystalline variety of sulphur, just like S_α at ordinary temperature. It does not pass to the α -form slowly or rapidly at the room temperature, like the monoclinic variety (S_β). We have examined S_ω after one year since its preparation and have found that the whole of it still remained insoluble in CS_2 and produced a system of diffraction rings exactly similar to those obtained in the case of a freshly prepared specimen.

It, therefore, appears that sulphur may exist at the ordinary temperature in two distinct crystalline states, namely, S_α and S_ω and both are highly stable. The mode of its preparation alone determines the state it assumes. It may, of course, be possible that one of the crystalline states is unstable. The rate of transformation of the unstable variety is extremely slow and can not easily be detected. For, it appears impossible that one and the same substance may exist in stable equilibrium in two different configurations (S_α and S_ω) under the same physical conditions. Sometimes impurities present in the mother substance influence its structure in such a way as to totally transform it. But at the present stage when the experimental evidences are quite meagre, no satisfactory conclusion can be arrived at about the real nature of S_ω .

4. THE TRANSITION OF S_ω INTO S_α AT HIGH TEMPERATURES

A quantity of white sulphur was heated at a temperature of about $88^\circ C$ for 36 hrs. and was analysed by X-rays at the room temperature. A pure S_α -pattern (Fig. 1) was obtained and the rings were quite sharp and narrow. The process of heating therefore, had completely modified the structure from the ω to the α -type. The α -modification so obtained was found to be quite stable at the ordinary temperature, as one should expect, and no sign of its reconversion was ever noticed.†

5. TRANSITION OF S_α INTO S_β BELOW THE MELTING POINT

As mentioned before (sec. 1b), we know from chemical literatures that orthorhombic sulphur is the only stable crystalline variety at the ordinary temperature,

* As white sulphur possesses a distinct crystalline structure different from that of S_α and S_β , we think it proper to represent it by a different symbol S_ω .

† The process of conversion of S_ω into S_α has recently been studied in greater detail. The results seem to throw a new light on the nature of S_ω and will be published in a future paper.

but it becomes unstable above 95°C . At this temperature and above it, orthorhombic sulphur passes slowly into a second crystalline phase (S_{β}) belonging to the monoclinic type. With a view to study the transition phenomenon, a cell of finely powdered orthorhombic sulphur was prepared and was maintained at a temperature of about 100°C during the exposure. But the photograph failed to furnish any evidence for the said transition phenomenon. A large number of exposures were made at temperatures varying between 90°C and 100°C and in every case, the pattern appeared highly irregular owing to the appearance of spots or dots, and long streaks (Figs. 12, 8 and 9). In most of the photographs no ring could be traced and the plates were full of blurred, or sharp spots. This peculiar phenomenon, although baffled our present endeavour, suggested another line of study and the results have been embodied in the next section (6). There we have come to the conclusion that the peculiar changes in the diffraction patterns are not at all associated with the transition phenomenon but are connected with the growth of the crystal size.

As it was found that the specimen when heated during the exposure, always exhibited dots, streaks, etc., and gave no idea of the transition from S_{α} to S_{β} , another method of enquiry was adopted. Thus in one of our experiments, the specimen was heated continuously to 100°C for about three days, which was long enough for the conversion of S_{α} into S_{β} . A small quantity of the heated specimen was quickly powdered* in a mortar and placed in the proper position for exposure at the room temperature.

Each exposed sample was replaced by a freshly prepared one after one hour. Though S_{β} is unstable at the ordinary temperature, yet the transformation of S_{β} into S_{α} does not take place very rapidly.¹⁸ This only produced a ring system exactly resembling that of rhombic sulphur (S_{α}). Similar experiments were performed with sulphur heated to higher temperatures (up to 100°C) for longer periods, and with quicker alteration of the exposed specimen but in no case any change in the ring system could be detected.

In another series of experiments, needles of monoclinic sulphur were first prepared by cooling molten sulphur in a crucible.¹⁸ Very fine shining needles projecting inwards from the walls of the vessel were obtained. Some of them were crushed in a mortar and examined at the room temperature. In this experiment the specimen was also changed every one hour during the exposure. The photograph showed exactly a S_{α} -pattern as mentioned in the previous paragraph. One is thus forced to the conclusion that either the period of conversion of S_{β} to S_{α} is shorter than the accepted period, or the process of powdering completely influences the conversion. From these experiments, no definite

* The powdering is essential for the appearance of continuous rings on the plate. If the specimen is first heated for a long time and then cooled to the room temperature, it only shows dots, streaks, etc. (see Sec. 6).

conclusion could be arrived at regarding the transition temperature of S_a to S_F in the solid state. Farther experiments are being conducted to elucidate this point.

6. SULPHUR AT HIGH TEMPERATURE, BUT BELOW THE MELTING POINT

It has been mentioned before (Sec. 5) that the ring system in the diffraction patterns of sulphur becomes very irregular when the specimen under examination is maintained at a high temperature during the exposure. With a view to study the phenomena systematically, several photographs were taken not only at different temperatures but also at each temperature the specimen was heated for different periods before the actual exposure. As a result, we have noticed that the special features characterising the patterns obtained at temperatures lying between 80°C and 110°C are (a) the discontinuity of the rings, (b) the appearance of asterism, *i.e.*, radial streaks, and (c) the appearance of a large number of sharp intense spots arranged irregularly on the plate. We have further observed that the nature of the pattern at any definite temperature depends again on the total period for which the specimen of sulphur is heated before the actual exposure.

As for example, three distinct stages of changes in the pattern were detected at 104°C . The first photograph (Fig. 12) was obtained with a specimen which was heated only during the period of exposure which was about ten hours. The figure shows very clear signs of asterism, specially in the central region of the photograph. The second stage of the pattern is illustrated in figure 8, where the specimen was heated for about thirty hours at 104°C before the exposure and the same temperature was maintained throughout the exposure. Here the asterism is less marked and the rings are distinctly broken or dotted in appearance (several intense spots appear on the plate) and all of them are not clearly separated. In the next photograph (Fig. 9) which was taken with the specimen heated for a period of sixty hours at 104°C , we see the last and the final stage of the pattern. This state persists for further periods of heating the exposed specimen, and it is characterised by the extreme sharpness of the intense spots on the photograph. They are now quite separated from one another and though they are arranged quite at random over the whole surface of the plate, yet they strongly resemble the spots in a Laue pattern in external appearance. The phenomenon of asterism persists up to the second stage but is never observed in this final stage.

Exactly similar experiments were repeated at different temperatures. We have noticed that the phenomenon of asterism is observed in a marked degree at higher temperature but it also appears at a temperature as low as 80°C , where it is very much less pronounced. Below 75°C we have not been able to detect

any asterism, although the grainy appearance of rings or the appearance of blurred intense spots is clearly revealed. At these lower temperatures again, the rings never disappear totally but only they are weak, and a number of spots appear on the plates. Some of the spots lie on the rings no doubt, but most of them are arranged in a disorderly manner. Recently we have observed these sharp spots even in the patterns of specimen at the room temperature 30°C , which was powdered a few days before the actual exposure.

It is quite evident from the above experiments that there must have been some sort of change taking place in the crystal texture of the powdered grains, when they are subjected to some heat treatment at high temperature. The first observation of the above peculiarities in the diffraction photographs at high temperatures was made at 100°C . This temperature was chosen with a view to study the phenomenon of enantiotropic transformation of sulphur, which is generally believed to take place above $95^{\circ}\cdot 5\text{C}$ (see Sec. 5). The appearance of asterism in the photograph at this temperature and also in others taken subsequently at various temperatures suggested that this effect might be due to some curvature of the lattice planes of the minute crystals in the powder, caused by the well known transformation strain which is produced homogeneously throughout each crystal at the time of transition from one crystalline phase to the other.¹⁹ The increased prominence of asterism with the increase of temperature generally supports the view. For a higher temperature in the case of enantiotropic structural transformation is equivalent to a greater force producing the strain. Moreover the total disappearance of asterism at lower temperatures gives further support of this view. But if this transformation strain is really responsible for asterism, then such transformation ($S_{\alpha} \rightarrow S_{\beta}$) can also take place at so low a temperature as 80°C where the phenomenon is clearly observed. But the existent literatures on sulphur do not support this latter point. According to them the structural transformation of sulphur does not take place below $95^{\circ}\cdot 5\text{C}$. D. Gernez²⁰ goes even further and according to him the transformation of S_{α} into S_{β} can not take place below the melting point, unless S_{α} is already admixed with a quantity of S_{β} and even in that case the transformation takes place at $97^{\circ}\cdot 6\text{C}$. F. Mitscherlich²⁰ was of opinion that the transition point lies in the proximity of the melting point of S_{α} .

Further if we assume that the transformation of S_{α} into S_{β} is possible even at these lower temperatures, still there are certain difficulties which are not clearly understood from this point of view. For example the strains produced during the process of structural transformation cannot account for (a) the discontinuity of the rings and (b) the appearance of innumerable sharp spots on the plates at the final stage of heating the exposed specimen. We shall see below that all the observations on sulphur here described find satisfactory explanations on the basis of the idea of growth of crystal-size at high temperatures.

To test the validity of the above idea we performed another experiment and results have confirmed this view. A quantity of finely divided sulphur was made into a thick paste with the help of collodion and a mixture of ether and alcohol. Allowing the paste to spread over a plane glass plate a film of sulphur-in-collodion was obtained. Inside the film, fine grains of sulphur remain embedded in the solid medium of collodion and are thus debarred from coming in contact and uniting together to form bigger crystals at higher temperatures. A suitable portion of the film was exposed at 104°C in the usual way and the pattern (Fig. 10) did not exhibit any peculiarity observed in the previous experiments. The nature of the pattern at 104°C was exactly similar to that at the room temperature.

7. THE PROCESS OF CRYSTAL GROWTH IN THE POWDERED GRAINS OF SULPHUR AT HIGHER TEMPERATURES

Evidences are now rife for the growth of bigger single crystals at sufficiently high temperatures from the polycrystalline aggregates of metals.²¹ The acceleration of crystal growth at higher temperatures has led to the idea that the increased thermal energy possessed by the molecules of the crystals in the form of kinetic energy, causes an increase of mobility of the molecules.²¹ This increased mobility is essential in the building up of bigger structures. For a small unit of crystal powder which we may assume to consist of a single crystal having some minute surface defects due to powdering, must be associated with other molecules or smaller units in the right positions and for this purpose even the molecules lying in the most favourable positions must possess sufficient freedom to move, so that their migration into the exact positions in the lattice may be possible.

Let us now consider a single grain which has a large number of similar immediate neighbours. The proper union between them resulting in a bigger single crystal must involve cementation of one unit with the other through faces which are crystallographically similar. When two such faces of the two neighbouring grains closely approach each other with their directions approximately parallel, a very favourable condition is created for their union into a bigger unit. The semi-crystalline layers of molecules covering each member of the growing particles will now bring about the union, forming themselves a sort of bridge-layer between them. This cement layer plays a very important part in the process of crystal growth in polycrystalline masses.²¹ In the first stage they remain in a more or less amorphous or semi-crystalline condition having a tendency for molecular alignment which is greatly helped by the increased mobility due to the rise in temperature. In the primary stage of development the grown-out-structure will behave as a highly imperfect single crystal owing partly to the approximate

parallelism of the uniting faces and partly due to the presence of the compromising semi-crystalline cement layer.

But as the period of heating continues these highly imperfect structures, on the one hand, associate themselves with other favourably oriented grains and thus grow into still bigger units while, on the other hand, the cement layer acts in such a way as to eliminate the defects present between two neighbouring faces. The gradual improvement of the order of perfection of the crystal is effected by the slow alignment of the molecules in the cement layer in a way demanded by the adjoining crystal faces. We may now imagine that, of the two adjoining faces, only one is absorbing the molecules available in the cement layer. This causes the consumption of the whole layer present at the beginning of the process. But really until the whole structure becomes truly perfect (certainly an ideal perfection is never realised) the boundary layer will never be totally absent. For as the layer loses one molecule by the process of alignment, another may be substituted there from the neighbouring face of the other unit, which is supposed to be inactive. Thus practically there is a continuous transport of molecules from one of the adjoining faces to the other, and the semi-crystalline layer is always present as a dynamically stable intermediate stage in the formation of big single crystals.

In an ideal condition when there are no impurities accumulating on the boundary layers²² retarding the function of the cement layer and when the rate of growth is fairly slow, we may expect an ideally perfect crystal by a long continuation of the process. But this ideal is hardly realised in practice and ultimately we are satisfied with a mosaic structure, which for all practical purposes serves as a good single crystal. Before actually interpreting our results with sulphur at high temperatures, we would like to present a picture of the diffraction phenomena including asterism as may be observed in the case of a crystal in its various stages of changes. Let us consider the diffraction pattern from a polycrystalline mass consisting of a number of single crystals distributed quite at random. In this case the pattern will evidently consist of a very large number of sharp Lane spots arranged in a disorderly manner.* If the constituent single crystals of the polycrystalline mass be now so fractured, as to be sub-divided into smaller units having their corresponding faces only slightly deviated from their original positions of accurate parallelism, the pattern will no longer exhibit any sharp spot, but will consist of radial streaks. For, just as the image of a luminous point formed by reflection from a plane mirror assumes the shape of a long streak (strictly a

* The number of crystals actually taking part in the diffraction should be very small such that it does not exceed, say, about 50. G. L. Clark has photographed the pattern due to polycrystalline aluminium sheets of various degrees of crystalline grain-size. The patterns of sulphur in the final stage of heating exactly resemble those of aluminium taken by Clark--.

See Bragg and Bragg, "The Crystalline State," Vol. I, p. 191.

highly eccentric ellipse), if the mirror is rotated in space with the normal lying within a small solid angle round its original position, so the Laue spots formed by reflection from the faces of the slightly orientated constituent units of the imperfect crystals will be elongated into streaks. Again, if these units are further disturbed or the diffracting units are powdered, so that the powdered grains are sufficiently small and their orientation is quite random, familiar Debye-Scherrer rings appear on the photographic plate.

The case of sulphur at high temperatures is very similar to the above case of the polycrystalline mass but the procedure is just the reverse. Here we start with a powdered specimen of sulphur which produces well defined Debye-Scherrer rings. With the increase of temperature, the minute single crystals begin to grow in size. In the first stage of the growth, the grown out structures remain highly imperfect, for the crystallographically similar faces of the component units are slightly deviated from one another with the results that continuous rings disappear and streaks or asterism come out prominently on the plate. With lapse of time, however, the imperfections of the grown out crystals gradually disappear and ultimately we arrive at a stage where the crystal grains become sufficiently perfect and large to produce sharp Laue spots of complicated nature. No streak may appear in this case.

In connection with the picture represented here above the growth of the crystal size, we like to reiterate the case of solidified plastic sulphur or the other types of sulphur which are not soluble in carbon disulphide (Sec. 3 F). The sizes of the crystals in these modifications are very small as they produce quite continuous rings without any further powdering the sample. This state is preserved until it is heated to a high temperature. It has been mentioned before that there is a strong evidence that a layer of SO_2 gas is formed and adheres to boundary surface of the grains of the insoluble sulphur modifications and this layer separates one unit from the other. If the sulphur molecules on the boundary possess sufficient kinetic energy to penetrate the SO_2 layer, then only growth may take place.²² At ordinary room temperature* evidently these sulphur molecules are not sufficiently mobile to pierce through the layer of SO_2 and thus bring about the growth in a manner discussed before. But as the temperature is raised, the layer of SO_2 gas is removed and then the growth commences in the usual way.

8. LIQUID SULPHUR (FIG. 16)

The work of Blatchford¹² on liquid sulphur at various temperatures has already been mentioned before (Sec. 1(d)). His investigation was carried out

* Distinct evidence of the growth of the sulphur powdered crystals which are soluble in CS_2 has been found even at the room temperature.

within the range of 130°C to 210°C . The arrangement only provided a small resolution and thus he observed only one diffraction band (Table IV) in the case of molten sulphur. With a narrower slit (0.4 m.m. diameter whereas the other author used a slit of 1.5 m.m. diameter) and a greater resolution two well defined rings have been observed. The spacings are recorded below :

TABLE IV.

Spacing $\times 10^8$.	Intensity.	114°C .	119°C .	128°C .	Blatchford ¹² (130°C)
d_1	w	4.96	5.14	4.90	$3.68 \pm .01$
d_2	S	3.42	3.51	3.45	

We confined our attention purposely below 130°C (the lowest temperature of Blatchford's experiment) with a view to study any structural difference between molten S_{α} and molten S_{β} . Rhombic S_{α} and monoclinic S_{β} sulphur were prepared in the usual way, and the liquid structure was examined just above the melting point, namely, 114°C (for S_{α}) and 119°C (for S_{β}) but no difference in the spacings calculated by the Bragg-relation could be detected.*

9. SULPHUR AT LOW TEMPERATURE

Preliminary investigation on S_{α} was carried out at the temperatures of CO_2 snow, mixture of CO_2 -snow and ether, and liquid oxygen. The powdered substance appeared perfectly white even at the temperature of CO_2 snow. The rings appeared sharper and better defined but hardly any difference in the structure could be detected.

The writer desires to express his thanks to Prof. B. B. Ray for his interest and helpful discussions in course of the work and also to Mr. K. Ray, M.Sc., for his valuable help during the experiment.

KHAIRA LABORATORY OF PHYSICS,
UNIVERSITY COLLEGE OF SCIENCE
92, UPPER CIRCULAR ROAD,
CALCUTTA.

* Recently further examination of liquid sulphur has been continued and the detailed result will be published in the next part.

Study of Sulphur Allotropes by the R-ray Diffraction Method 181

REFERENCES

- ¹ P. Groth—*Chemische Kristallographie*, **1**, pp. 23 and 26 (1906)
- ² W. Bragg—*Proc. Roy. Soc. (A)*, London, **89**, 575 (1914).
- ³ Mark and Wigner—*Zell. f. Phys. Chem.*, **111**, 308 (1921).
- ⁴ Warren and Burwell—*Jour. Chem. Phys.*, **3**, 6 (1935).
- ⁵ P. Groth—*loc. cit.*, **1**, pp. 23 and 28.
- ⁶ (a) J. R. Partington, *A Text Book of Inorganic Chemistry* (1930), p. 491.
(b) Mellor—*Modern Inorganic Chemistry* (1919), p. 491.
- ⁷ J. R. Partington—*loc. cit.*, p. 491.
- ⁸ " " "
- ⁹ " " p. 490.
- ¹⁰ *Comptes Rendus*, **192**, 557 (1931).
- ¹¹ Muthmann—*Zeit. f. Krist.*, **17**, 336 (1890).
P. Groth, *loc. cit.*, **1**, pp. 26 and 28.
- ¹² A. H. Blatchford—*Proc. Phys. Soc.*, **45**, 493 (1933).
- ¹³ Bragg—*The Crystalline State*, **1** (1933), p. 191.
- ¹⁴ Randall—"The Diffraction of X-rays and electrons by amorphous solids, liquids and gases" (1931), p. 28.
- ¹⁵ P. Scherrer—"Nachr. Göttingen Gesell." (1918), p. 98.
- ¹⁶ Brill—*Zeit. f. Krist.*, **68**, 387 (1928).
- ¹⁷ J. R. Partington, *loc. cit.*, p. 498.
- ¹⁸ Mellor—*loc. cit.*, p. 396.
- ¹⁹ W. G. Burgers—"International Conference on Physics (London)" The Physical Society papers and discussions, Vol. II (1934), p. 158.
- ²⁰ Mellor—"Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X.
- ²¹ Wheeler P. Davey—"A Study of Crystal Structure and its Applications," p. 377 (1934), McGraw-Hill Book Company, Ltd., New York and London.
- ²² Wheeler P. Davey—*loc. cit.*, p. 378 and G. Tammann—"A Text book of Metallurgy," Chemical Catalog Company, New York (1925).
- ²³ J. T. Randall—*loc. cit.*, p. 212.
- ²⁴ Katz—*Naturwiss.*, **13**, 411 (1925).
- ²⁵ Mark and Susich—*Koll. ZS*, **46**, 11 (1928).

SPACE-GROUP OF CREATININE

By K. BANERJEE, D.Sc.

Reader in Physics, Dacca University

AND

ABDUL HAQUE, M.Sc.

Imperial College of Science and Technology, London

(Received for publication, April 2, 1958.)

ABSTRACT. The cell dimensions of creatinine has been determined by the rotation photograph method with results, $a_0 = 14.86 \text{ \AA}$, $b_0 = 13.14 \text{ \AA}$, $c_0 = 5.85$ and $\beta = 110^\circ 36'$. The number of molecules per unit cell is thus calculated to be 8. From oscillation photographs it is concluded that no systematic absence of planes occur and hence the space-group is found to be $C^{12}_2/P/m$.

The recent works by Bernal and his collaborators have given a great impetus to X-ray investigations of substances of biological origin, as such studies have yielded results which have been found very useful in the elucidation of constitution of these substances. In fact, in the case of ergosterol, the original formula proposed for this compound had to be modified in view of the results of Bernal. But the molecules of such compounds are too large for the determinations of their atomic arrangements by X-ray investigations on them. In order to get a clue into the structure of the molecules of these compounds, it will be more useful to determine the structures of smaller units of which these large molecules are composed. The molecules of biological products are mostly composed of reduced carbon rings and a few types of heterocyclic rings. So the proper procedure for such investigations is to determine correctly the structure of such simple rings and apply that knowledge to determine the structures of the more complicated molecules. Creatinine is such a simple heterocyclic ring compound and since good single crystals of this substance are easily obtained, and as this substance itself has a great biological interest, so it has been chosen for our investigations. In the present communication is described the determination of its space-group and attempts are being made to make a Fourier analysis of its structure. Crea-

nine has been found to belong to the monoclinic prismatic class, with axial angle $110^{\circ} 36'$ (Kopp, Groth's *Chemische Kristallographie*, Vol. III, p. 576). Its axial ratio as given in Groth's book is $1.1571 : 1 : ?$

The pure substance was crystallised from water. Monoclinic prisms bounded by a combination of m (110), c (001) and a (100) faces were found. In some crystals, an end face (102) was also developed.

For the determination of the dimensions of the unit cell rotation photographs about the three crystallographic axes a , b , c , were taken.

The axial lengths were found to be :—

$$a_0 = 13.14 \text{ \AA}, \quad b_0 = 5.85 \text{ \AA} \quad \text{and} \quad c_0 = 14.86 \text{ \AA}.$$

The density of creatinine was determined by floatation method from a mixture of chloroform and acetone with proper correction of temperature and it was found to be 1.386 gms. per c.c. Hence the number of creatinine molecules per unit cell comes out to be 8.

Oscillation photographs about the two inclined a and c axes are taken. As the two axes lie in a plane of symmetry only nine photographs at intervals of 10° were taken. The reflecting planes were identified in the usual way and the results are collected together in the table below. By examining the list of planes it is found that there is no systematic absence of planes. So the space-group is $C_{2h}^1/P2_1/m$.

TABLE I.

List of reflecting planes of creatinine (photographs taken about the two inclined a and c axes).

Axial Planes.

Planes.	Estimated intensity.	Planes.	Estimated intensity.
002	V.S.	090	V.S.
004	W.	0(11)0	S.
020	V.S.	0(12)0	V.W.
050	M.S.	400	S.
060	W.	800	V.W.
080	M.W.	(10)00	M.W.

TABLE II.

Prism Planes.

Planes.	Intensity.	Planes.	Intensity
012	S.	401	V.S.
014	V.W.	402	V.S.
022	V.S.	601	V.V.W.
023	V.S.	601	W.
025	V.V.W.	801	W.
041	V.S.	801	V.S.
042	W.	1201	S.
043	M.S.	(12)01	S.
051	S.	(13)01	V.W.
054	V.V.W.	(13)01	V.W.
063	V.W.	(14)02	W.
071	M.W.	(16)02	W.
081	V.W.	(17)01	V.V.W.
091	M.W.	120	V.S.
092	M.W.	130	M.W.
0(10)1	W.	140	V.S.
0'11)2	V.V.W.	150	S.
0(11)3	V.W.	160	M.S.
0(12)1	M.W.	170	M.W.
0(12)2	M.W.	180	V.V.W.
0(14)1	V.W.	190	V.W.
101	V.S.	1(10)0	W.
102	V.S.	1(11)0	M.W.
102	V.V.W.	1(12)0	W.
103	W.	1(14)0	M.W.
201	V.S.	230	V.W.
202	S.	240	S.
203	W.	250	S.

TABLE II (contd.).

Prism Planes.

Planes.	Intensity	Planes.	Intensity.
260	V.S.	590	M.S.
270	V.S.	5(12)0	M.S.
290	V.W.	5(13)0	V.W.
2(10)0	V.W.	610	V.S.
2(12)0	M.S.	620	M.W.
2(16)0	V.W.	630	S.
320	W.	640	M.W.
330	V.S.	660	M.W.
340	V.S.	670	V.S.
360	M.S.	690	V.V.W.
370	V.S.	6(11)0	W.
380	M.W.	710	M.W.
3(10)0	M.S.	730	M.S.
3(11)0	M.W.	740	M.S.
3(12)0	M.S.	750	S.
3(14)0	W.	760	V.W.
3(16)0	M.W.	770	S.
440	V.W.	810	S.
460	V.S.	830	V.S.
480	M.W.	850	V.V.W.
490	V.W.	870	M.W.
4(11)0	M.	880	V.W.
4(12)0	M.W.	8(10)0	V.W.
510	V.V.W.	8(11)0	S.
520	M.S.	8(13)0	M.W.
530	M.W.	8(14)0	V.W.
540	V.W.	920	M.W.
550	W.	980	M.W.
570	S.	990	S.
580	V.S.	9(11)0	V.W.

TABLE II (contd.).

Prism Planes.

Planes.	Intensity.	Planes.	Intensity.
9(14)0	M.W.	(13)40	M.W.
(10)10	M.W.	(13)60	V.V.W.
(10)40	M.W.	(13)70	V.V.W.
(10)60	M.W.	(13)90	S.
(10)70	S.	(14)60	V.V.W.
(11)20	M.W.	(14)70	M.W.
(11)60	V.S.	(15)30	W.
(11)90	M.S.	(15)50	M.W.
(11)(10)0	M.S.	(15)90	W.
(12)10	S.	(16)10	W.
(12)40	V.S.	(16)30	W.
(12)60	M.W.	(16)40	M.W.
(13)10	W.	(17)20	V.W.
(13)20	W.	(17)30	V.V.W.

TABLE III.

General Planes.

Planes.	Intensity.	Planes.	Intensity.
111	V.S.	13 ¹	S.
111 ⁻	V.S.	13 ¹	V.S.
112	S.	13 ²	M.S.
112 ⁻	V.S.	13 ⁴	W.
114	M.W.	13 ⁵	W.
121	M.S.	14 ¹	V.W.
121 ⁻	M.S.	14 ²	M.W.
123	M.W.	15 ¹	V.S.

TABLE III (contd.)

General Planes.

Planes.	Intensity.	Planes.	Intensity.
151	V.S.	1 (13) $\bar{1}$	M. W.
152	V.S.	1 (13) 2	W.
152	V.S.	1 (13) $\bar{2}$	M. W.
153	V.W.	211	V. S.
161	S.	21 $\bar{1}$	V. S.
161	S.	212	V. S.
162	S.	213	V. S.
163	V.W.	214	W.
171	S.	22 $\bar{1}$	V. S.
17 $\bar{1}$	S.	222	M. S.
172	V.V.W.	223	M. S.
172	V.S.	22 $\bar{4}$	W.
173	V.V.W.	231	V. S.
174	W.	23 $\bar{1}$	S.
181	W.	232	V. W.
182	M.W.	232	V. V. W.
191	W.	233	S.
1 (10) 1	M.W.	234	V. W.
1 (10) 2	M.W.	241	M. W.
1 (10) $\bar{2}$	M.W.	241	V. W.
1 (11) 1	M.S.	242	M. S.
1 (11) $\bar{1}$	M.S.	242	V. S.
1 (11) 2	V.V.W.	245	M. W.
1 (11) $\bar{2}$	W.	251	S.
1 (12) 1	V.V.W.	25 $\bar{1}$	S.
1 (12) 1	V.V.W.	252	S.
1 (12) $\bar{2}$	V. S.	252	V. S.
1 (13) 1	M. W.	253	M. S.

TABLE III (contd.).

General Planes.

Planes.	Intensity	Planes.	Intensity.
254	V V.W.	321	V S.
261	M.S.	322	S.
262	W.	322	S.
262	V.V.W.	333	M.S.
263	V.W.	341	M.S.
271	V.V.W.	341	S.
271	S.	342	V.S.
272	V.W.	344	S.
272	V.W.	343	V.V.W.
273	V.W.	351	M.S.
274	V.W.	351	M.S.
274	M.W.	353	V.V.W.
281	S.	354	W.
281	S.	354	W.
282	M.S.	361	M.S.
291	V.V.W.	361	W.
292	M.W.	362	V.S.
2(10)1	V.W.	363	M.S.
2(10)2	M.S.	371	M.S.
2(10)2	M.S.	371	M.S.
2(11)1	M.W.	372	W.
2(11)1	V.V.W.	372	M.W.
2(13)2	M.S.	381	M.S.
2(16)1	V.V.W.	381	M.S.
311	V.S.	382	V.W.
311	V.S.	382	V.V.W.
212	S.	391	M.S.
313	M.S.	391	V.V.W.
313	W.	392	W.

TABLE III (contd.).

General Planes.

Planes.	Intensity.	Planes.	Intensity.
$39\bar{2}$	V.V.W.	$41\bar{3}$	M.S.
$3(10)1$	M.S.	$45\bar{1}$	V.S.
$3(10)\bar{2}$	M.S.	$45\bar{1}$	V.S.
$3(10)\bar{2}$	W.	$45\bar{2}$	W.
$3(12)1$	W.	$45\bar{2}$	V.W.
$3(12)\bar{2}$	W.	$45\bar{3}$	W.
$3(13)2$	V.V.W.	$45\bar{4}$	V.V.W.
$3(14)1$	V.V.W.	$46\bar{1}$	W.
$3(15)1$	V.V.S.	$46\bar{1}$	S
$3(15)\bar{1}$	V.V.S.	$46\bar{2}$	M.S.
$41\bar{1}$	V.W.	$46\bar{2}$	S.
$41\bar{1}$	V.W.	$47\bar{1}$	M.W.
$41\bar{2}$	V.S.	$48\bar{1}$	M.S.
$41\bar{2}$	V.S.	$48\bar{2}$	M.W.
$41\bar{3}$	M.W.	$48\bar{3}$	V.M.
$41\bar{3}$	M.S.	$49\bar{1}$	M.S.
$41\bar{6}$	W.	$49\bar{2}$	W.
$41\bar{6}$	M.S.	$4(10)1$	W.
$42\bar{1}$	V.S.	$4(10)\bar{1}$	M.W.
$42\bar{1}$	V.S.	$4(10)2$	S.
$42\bar{2}$	V.W.	$4(10)\bar{2}$	V.S.
$42\bar{4}$	V.V.W.	$4(11)1$	W.
$43\bar{1}$	V.S.	$4(11)\bar{1}$	V.V.W.
$43\bar{1}$	V.S.	$4(11)2$	M.S.
$43\bar{2}$	S.	$4(12)1$	V.W.
$43\bar{4}$	V.V.W.	$4(13)1$	V.V.W.
$44\bar{1}$	M.S.	$4(13)\bar{1}$	V.V.W.
$44\bar{2}$	V.V.W.	$4(15)1$	V.V.W.
$44\bar{3}$	V.V.W.	$4(15)\bar{1}$	V.V.W.

TABLE III (contd.).

General Planes.

Planes.	Intensity.	Planes.	Intensity.
511	V.S.	612	V.S.
512	V.S.	621	M.S.
51 $\bar{2}$	V.V.S.	622	S.
521	M.S.	62 $\bar{2}$	S.
52 $\bar{1}$	M.S.	632	W.
52 $\bar{2}$	M.S.	63 $\bar{2}$	W.
531	M.S.	642	M.W.
53 $\bar{1}$	M.S.	64 $\bar{2}$	M.W.
53 $\bar{2}$	V.S.	651	V.W.
541	W.	65 $\bar{1}$	V.W.
54 $\bar{1}$	W.	661	M.S.
551	V.V.W.	66 $\bar{1}$	M.W.
55 $\bar{2}$	V.S.	671	V.W.
55 $\bar{2}$	V.S.	67 $\bar{1}$	M.S.
562	V.V.W.	672	V.W.
56 $\bar{2}$	V.V.W.	67 $\bar{2}$	V.V.W.
572	V.V.W.	6(10)1	S.
57 $\bar{2}$	V.V.W.	6(10) $\bar{1}$	M.S.
581	S.	6(11)2	S.
591	M.W.	6(11) $\bar{2}$	V.W.
59 $\bar{1}$	M.W.	6(12)1	W.
592	M.S.	6(13)1	M.W.
5(10)2	M.S.	6(13) $\bar{1}$	M.W.
5(10) $\bar{2}$	V.V.W.	6(14)1	V.W.
5(12)1	V.W.	6(14) $\bar{1}$	V.V.W.
5(13) $\bar{2}$	V.V.W.	6(15)1	V.V.W.
611	V.S.	6(15) $\bar{1}$	V.V.W.
61 $\bar{1}$	V.S.	711	M.S.
612	V.S.	71 $\bar{1}$	M.S.

TABLE III (contd.).

General Planes.

Planes.	Intensity.	Planes.	Intensity.
721	M.W.	841	S.
72 $\bar{1}$	M.W.	841	S.
722	M.S.	891	V.V.W.
731	S.	89 $\bar{1}$	V.W.
73 $\bar{1}$	S.	892	W.
732	M.W.	892	W.
742	M.W.	8(14)1	V.V.W.
74 $\bar{2}$	M.W.	8(14) $\bar{1}$	V.V.W.
752	W.	912	V.W.
75 $\bar{2}$	V.W.	91 $\bar{2}$	V.W.
761	M.S.	931	M.S.
76 $\bar{1}$	M.S.	93 $\bar{1}$	M.S.
781	W.	932	M.W.
78 $\bar{1}$	W.	932	M.S.
791	M.S.	952	M.W.
79 $\bar{1}$	M.S.	95 $\bar{2}$	W.
7(10)1	V.S.	961	V.W.
7(10) $\bar{1}$	V.W.	96 $\bar{1}$	V.V.W.
7(12)1	M.S.	971	V.W.
7(12) $\bar{1}$	M.W.	97 $\bar{1}$	V.W.
811	V.S.	992	V.W.
81 $\bar{1}$	V.S.	9(11)2	S.
812	V.S.	9(13)1	M.S.
81 $\bar{2}$	V.S.	9(13) $\bar{1}$	M.W.
821	M.S.	(10)1 $\bar{1}$	S.
831	W.	(10)12	V.W.
83 $\bar{1}$	W.	(10)1 $\bar{2}$	W.
832	M.W.	(10)21	M.W.
83 $\bar{2}$	W.	(10)2 $\bar{1}$	M.S.

TABLE III (contd.).

General Planes.

Planes.	Intensity.	Planes.	Intensity.
(10)42	M.S.	(11)(10)2	W.
(10)4 $\bar{2}$	M.W.	(11)(12)1	M S
(10)52	V.V.W.	(12)21	S.
(10)61	M.S.	(12)21	S
(10)6 $\bar{1}$	V V.W.	(12)22	V.W.
(10)81	V.V.W.	(12)2 $\bar{2}$	V.V.W
(10)9 $\bar{1}$	V.V.W.	(12)42	W.
(10)92	V.W.	(12)51	M.W.
(10)(10)1	V.W.	(12)62	V.V.W.
(10)(13)1	M.W.	(12)62	V.V.W.
(10)(13)1	V.V.W.	(12)72	M.S.
(11)11	M.W.	(12)7 $\bar{2}$	M.S.
(11)1 $\bar{1}$	M.W.	(12)82	W.
(11)2 $\bar{1}$	W.	(12)9 $\bar{1}$	V.V.W.
(11)22	M S.	(12)(10)2	V.W.
(11)22	M.S.	(12)(12)1	M.W.
(11)5 $\bar{1}$	M.W.	(12)(12)1	V.V.W.
(11)52	V.V.W.	(13)11	M.S
(11)61	V.W.	(13)1 $\bar{1}$	V.W.
(11)61	V W.	(13)21	V.W.
(11)62	V.V.W.	(13)2 $\bar{2}$	M.S.
(11)72	V.W.	(13)31	V.W.
(11)81	V.V W	(13)3 $\bar{1}$	M.W.
(11)8 $\bar{2}$	V V.W.	(13)32	M W.
(11)91	V.W.	(13)32	M.W.
(11)9 $\bar{1}$	V.V.W.	(13)41	V.V.W.
(11)92	V.W.	(13)41	V.V.W.
(11)9 $\bar{2}$	M S.	(13)42	M.W.
(11)(10)2	M.W.	(13)52	W.

TABLE III (contd.).

General Planes.

Planes.	Intensity.	Planes	Intensity
(13)5 ²	M.W.	(14)8 ¹	V.W.
(13)6 ¹	M.S.	(15)11	V.V.W.
(13)6 ¹	M.S.	(15)3 ¹	V.V.W.
(13)7 ¹	V.V.W.	(15)3 ¹	V.W.
(13)7 ²	M.W.	(15)4 ¹	M.W.
(13)7 ²	M.W.	(15)4 ²	W.
(13)9 ¹	V.W.	(15)5 ¹	M.W.
(13)9 ¹	M.W.	(15)5 ¹	M.W.
(14)1 ²	V.V.W.	(15)6 ¹	V.V.W.
(14)2 ¹	M.W.	(15)7 ¹	V.V.W.
(14)2 ¹	V.W.	(15)7 ¹	V.V.
(14)2 ²	W.	(15)8 ¹	V.W.
(14)2 ²	W.	(15)8 ¹	V.W.
(14)4 ¹	M.W.	(16)11	V.V.W.
(14)4 ¹	M.W.	(16)21	V.V.W.
(14)5 ¹	V.V.W.	(16)21	V.V.W.
(14)5 ¹	V.W.	(16)3 ¹	M.W.
(14)6 ¹	V.W.	(16)3 ¹	M.W.
(14)6 ¹	V.W.	(16)4 ¹	V.V.W.
(14)7 ¹	M.W.	(16)4 ¹	V.V.W.
(14)7 ¹	M.W.	(16)6 ¹	V.V.W.
(14)7 ²	M.W.	(16)6 ¹	V.V.W.
(14)8 ¹	V.W.	(17)3 ¹	M.W.

DETERMINATION OF THE FREQUENCY OF AN OSCILLATOR WITH A CONDENSER

BY H. MUKHERJEE

(Received for publication, April 28, 1938.)

ABSTRACT. With an a. c. galvanometer of the form of a watt-meter or a dynamometer null point is obtained under two conditions, namely, (1) when the current through either the fixed or the moving coil is zero and (2) when the phase difference between the currents in the two systems of coils is 90° . In the method described below, advantage is taken of the second condition. The resistances and the condenser are arranged in the arms of a Wheatstone net, the moving coil in one of the diagonal arms and the fixed coils in series with the current source in the other diagonal arm. It is shown that the phase-difference between the currents in the two systems of coils is 90° when

$$\frac{I}{C^2 p^2} = \frac{Q}{P} R \left\{ R + \frac{G(P+Q)}{P+Q+G} \right\}.$$

INTRODUCTION

When a dynamometer or a watt-meter is used as a recording instrument for alternating currents, the deflection of its moving coil is given by

$$\delta = A \cdot I_f I_m \cos \chi$$

where I_f , I_m are the R. M. S. values of the currents in the fixed and moving coils respectively and χ , the phase difference between them. It is obvious that the deflection is one way or the other according as $\cos \chi$ is positive or negative and is zero when (1) I_f or $I_m = 0$ or (2) $\chi = \frac{\pi}{2}$. In experiments which require the fulfilment of the first condition such an instrument can be used in place of telephones. In the experiment described below, however, the null point is due to the fulfilment of the second condition.

THEORY

A system consisting of a resistance R and a reactance X acts with respect to an alternating current as an impedance of value $R + jX$. If the reactance is inductive, $X = Lp$, where L = inductance and $p = 2\pi \cdot \text{frequency}$; if the reactance is capacitive, $X = -\frac{1}{Cp}$, where C = capacity.

In figure 1, the impedances of the arms ab , bc and ad consist of the non-inductive resistances P , Q and R respectively while the impedance of the arm cd is $-\frac{j}{Cp}$. The arm ac contains the moving coil of an a.c. galvanometer of the form of a vertical watt-meter or a dynamometer. Assuming the inductance of the moving coil to be zero, the impedance of this arm is the resistance, G . Let i_1 , i_2 , etc., be the currents in the different parts of the network at any instant. Then

$$\left. \begin{aligned} i &= i_1 + i_3 \\ i_2 &= i_1 - i_g \\ i_4 &= i_3 + i_g \end{aligned} \right\} \quad \dots (1)$$

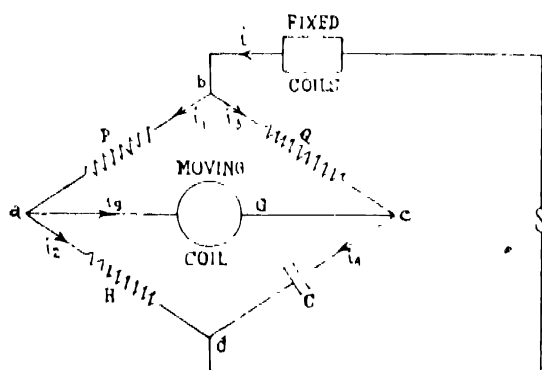


FIGURE 1.

In the mesh $abca$

$$Gi_g - Qi_3 + Pi_1 = 0 \quad \dots (2)$$

and in the mesh bcd

$$Gi_g - \frac{j}{Cp} i_4 - Ri_2 = 0$$

or

$$(R + G + jX)i_g + jXi_3 - Ri_1 = 0 \quad \dots (3)$$

where

$$X = -\frac{j}{Cp}$$

From (1), (2) and (3)

$$\begin{aligned} \frac{i_g}{QR - jPX} &= \frac{i_3}{P(R + G + jX) + RG} = -\frac{i_1}{Q(R + G + jX) + jXG} \\ &= \frac{i}{R(P + Q + G) + G(P + Q) + jX(P + Q + G)} \end{aligned}$$

$$\text{or} \quad \frac{i_{\theta}}{P\left(\frac{Q}{P}R - jX\right)} = \frac{i}{(P+Q+G)\left\{R + \frac{G(P+Q)}{P+Q+G} + jX\right\}}$$

$$\text{or} \quad \frac{i_{\theta}}{i} = \frac{P}{P+Q+G} \frac{\sqrt{\frac{Q^2}{P^2}R^2 + X^2}}{\left\{R + \frac{G(P+Q)}{P+Q+G}\right\}^2 + X^2} e^{-j(\phi+\theta)} \quad \dots (4)$$

$$\begin{aligned} \text{where} \quad \tan \phi &= \frac{X}{\frac{Q}{P}R} \\ \text{and} \quad \tan \theta &= \frac{X}{R + \frac{G(P+Q)}{P+Q+G}} \end{aligned} \quad \dots (5)$$

Thus the phase difference between i_{θ} and i is $\phi + \theta$. The deflection of the moving coil will, therefore, be zero if

$$\phi + \theta = \frac{\pi}{2}$$

$$\text{or} \quad \tan \phi = \cot \theta$$

$$\text{or} \quad \frac{X}{\frac{Q}{P}R} = \frac{R + \frac{G(P+Q)}{P+Q+G}}{X}$$

$$\text{or} \quad X^2 = \frac{1}{C^2 p^2} = \frac{Q}{P}R \left\{R + \frac{G(P+Q)}{P+Q+G}\right\} \quad \dots (6)$$

In deducing the above equation, the inductance of the moving coil has been assumed to be zero. In practice, however, that is not the case. The inductance should therefore, be compensated by a preliminary experiment from which the resistance, G , of the moving coil arm will also be obtained. The connections for the purpose are given in figure 2.

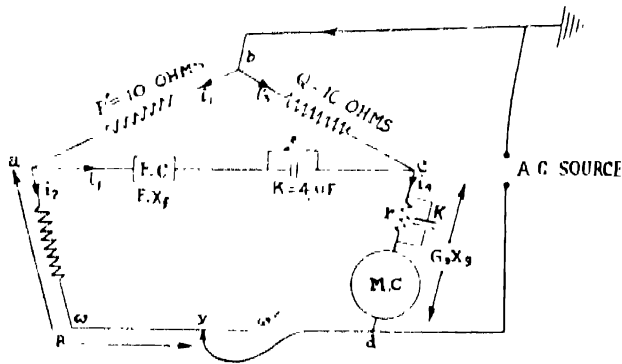


FIGURE 2.

If P' and G are the resistances, X_f and X_g , the reactances of the arms ac and cd respectively,

$$P'i'_1 + (P' + jX_f)i'_f - Q'i'_3 = 0$$

or $(P' + Q' + P' + jX_f)i'_f - Q'i'_3 + P'i'_2 = 0$

and $(P' + jX_f)i'_f + (G + jX_g)i'_4 - R'i'_2 = 0$

whence
$$\frac{Q'R' - P'G - jP'X_g}{Q'i'_f - P'G - jP'X_g} = \frac{i'_4}{R'(P' + Q') + P'(P' + R') + jX_f(P' + R')}$$

The phase difference between i'_f and i'_4 is $\theta' + \phi'$, where

$$\tan \theta' = \frac{X_f}{P' + \frac{R'(P' + Q')}{P' + R'}}$$

and
$$\tan \phi' = \frac{X_g}{\frac{Q'}{P'} R' - G}$$

There will be no deflection if $\theta' + \phi' = \frac{\pi}{2}$, or $\tan \phi' = \cot \theta'$

or
$$X_f X_g = \left(\frac{Q'}{P'} R' - G \right) \left\{ P' + \frac{R'(P' + Q')}{P' + R'} \right\} \quad \dots (7)$$

There will also be no deflection if $i'_f = 0$, the conditions for which are

$$\left. \begin{aligned} \frac{Q'}{P'} R' &= G \\ X_g &= 0 \end{aligned} \right\} \quad \dots (8)$$

and

It is easy to see that

$$X_g = L_g P - \frac{r^2 k p}{1 + r^2 k^2 p^2}$$

where L_g = inductance of the moving coil, so that

when $X_g = 0$

$$L_g = \frac{r^2 k}{1 + r^2 k^2 p^2} \quad (9)$$

EXPERIMENT

(i) *Arrangement for securing constancy of frequency* :—Since in most cases the frequency of an audio oscillator depends on the strength of the current drawn in the experimental circuit, the device shown in figure 3, may be adopted to ensure constancy of the frequency.

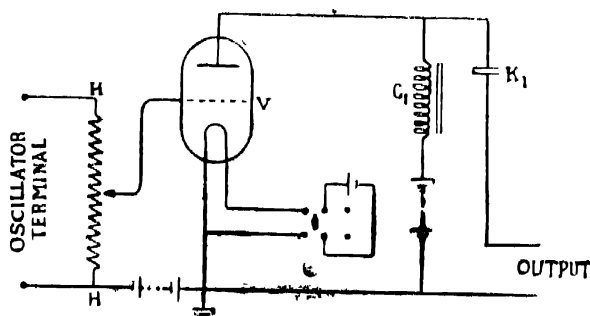


FIGURE 3.

V→Valve having an internal resistance less than 300 ohms. It may be of type Philips F 406 or Mazda Ac/P1.

H→High resistance potentiometer.

C₁→Low frequency choke of valve 20 to 100 henries.

K₁→Condenser of capacity 2 to 8 μF.

t→Mercury cup key intended to let the output current flow only as long as necessary.

(ii) *Adjustment of the position of the moving coil* :—When using a galvanometer of the watt-meter or dynamometer type for a. c. measurements, the initial position of the moving coil should be carefully adjusted. If the position is not symmetrical with respect to the fixed coils, there will be a linking between the moving coil and the lines of force due to a current in the fixed coils and if this current is alternating, there will be an induced current in the moving coil tending

to bring it to the symmetrical position. To start with, therefore, the levelling screws and the torsion head should be adjusted so that the moving coil may be symmetrically placed with respect to the fixed coils. The former is then short-circuited and a fairly high alternating current sent through the latter. If there is a deflection, the torsion-head should be turned in the direction of the deflection till the moving coil remains unaffected by the current in the fixed coils.

(iii) *Compensation of the moving coil*:—The arrangement of the apparatus is shown in figure 2. The balance corresponding to equation (7) is easily obtained for any value of r simply by adjusting R' . After obtaining such a balance, the condenser K is short-circuited to alter the phase difference between i'_r and i'_r . The balance will be disturbed. The procedure is repeated with different values of r till there is no deflection whether K is short-circuited or not, i.e., till the balance is independent of the reactance of the arm ac . The co-efficient of X_r must then be zero, i.e.,

$$X_y = 0$$

and therefore, (since $Q' = P'$)

$$R' = G.$$

The resistance of the part, xy , together with that of the connecting wires in the R' -arm is determined in the manner described in (V).

(iv) *Arrangement for the Determination of Frequency*:—The fixed coil and the compensated moving coil are now connected as in figure 4, and with the standard condenser C in the fourth arm, cd , of the network, R is adjusted till balance.

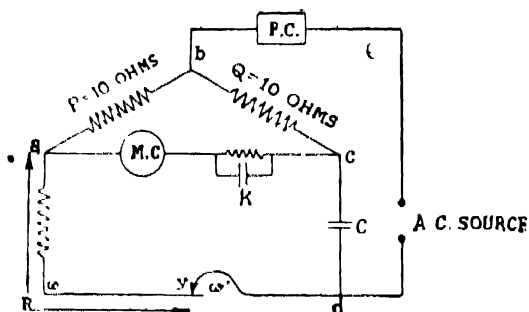


FIGURE 4.

(v) *Determination of the Unknown Parts of the Resistance of the Arm ad :—*

The unknown parts of the resistance of the R-arm (fig. 4) or the R'-arm (fig. 2) are the resistance of the connecting wires and that of the wire $w w'$ between the end w and the final balance point y . In order to determine the total value of these resistances, the *a. c.* source is replaced by a *d. c.* source in the last arrangement and the ratio Q/P made equal to 100. The known resistances in the part $a w$ are all plugged. Instead of the condenser, C , a resistance box is put in the arm, $c d$, and the resistance of this arm adjusted for balance at the final null points obtained in (iii) and (iv).

REMARKS

In selecting the values of the resistances P and Q for experiment (iv) two points are to be borne in mind.

(a) It will be noticed from equation (4) that the ratio i_a/i depends on the fraction $\frac{P}{P+Q+G}$. This fraction should, therefore, not be too small, otherwise the sensitivity of the arrangement will be affected.

(b) From equation (6) it will be seen that the accuracy of the result depends among other things on the quantity $\frac{G(P+Q)}{P+Q+G}$. Now G is determined by a separate experiment; hence in order that any error introduced in its determination may not appreciably affect the result, $(P+Q)$ should be suitably small in comparison with G .

In the experiment conducted in this laboratory, the value of G after the compensation of the moving coil was 136 ohms. Hence keeping the two points mentioned above in view P and Q were each made equal to 10 ohms.

It is obvious that the oscillator used must give a sinuous *e.m.f.* or be one in which the harmonics have a very low intensity. A Vreeland oscillator or a carefully constructed valve oscillator is very suitable.

It is also possible to determine the frequency with the help of an inductance instead of a capacity—the formula in this case will be

$$L^2 h^2 = \left\{ \frac{Q}{P} R - S \right\} \left\{ R + S + \frac{G(P+Q)}{P+Q+G} \right\}$$

where L = inductance and S = resistance of the arm containing it. But in this case, unless L is fairly large (*i.e.*, about 10 *m. h.* or more), $\left(\frac{Q}{P} R - S \right)$ is small and so the error in the determination is comparatively large.

The method of compensating an inductance described above is known as Sumpner's method. The effective resistance of the system consisting of the condenser, k , and the resistance, r , (fig. 2) is $\frac{r}{1 + r^2 k^2 p^2}$ and the effective

reactance $= \frac{r^2 k p}{1 + r^2 k^2 p^2}$. Thus by choosing a suitable condenser, the compensation can be made practically independent of the frequency of the oscillator up to 1000 cycles per sec. The inductance of the moving coil of the galvanometer used in this laboratory was about 0.36 m.h. The condenser chosen had, therefore, a capacity of 0.03 μ F.

Once the moving coil is carefully compensated, the galvanometer can be used to determine frequencies covering a wide range within error of 1% in 3000. Conversely if the frequency is known, the method affords means of determining capacities quickly and accurately.

For determination of inductances, the method is more convenient than Wien's method in that it entails an economy of apparatus and time—provided that the compensating system is regarded as a part of the galvanometer—while the accuracy of the result obtained is not less.

I am highly grateful to Prof. S. N. Bose for his material help in developing the method.

PHYSICS DEPARTMENT,
DACCA UNIVERSITY.

MAGNETO-RESISTANCE CHANGE OF FERROMAGNETICS IN ALTERNATING MAGNETIC FIELD

By S. SHARAN, M.Sc. (Pat.)

Lecturer, Bihar College of Engineering, Patna

(COMMUNICATED BY PROF. K. PROSAD)

(Received for publication April 4 1938.)

ABSTRACT. The resistances of nickel and Ni iron permalloy have been studied under the effect of an alternating magnetic field alone and also under the effect of an alternating and a direct magnetic field simultaneously. It has been observed that the application of a gradually increasing alternating field in the absence of a direct field produces no change in the resistance of the specimen, until it has a value equal to the coercive field of the specimen ; and if the alternating field is increased beyond this value the resistance increases in the same way as it does in the case of the direct field. In the presence of a direct field, the alternating field first causes a decrease in the resistance and after a certain value has been reached, corresponding to which the resistance is minimum, the resistance begins to increase as usual. A definite relation has been observed between this particular value of the alternating field and the direct field. Further, it has been observed that the resistance of the specimen increases beyond its original value at zero alternating field, only when the alternating field is greater than the sum of the direct field and the coercive field of the specimen. Theoretical explanation of the above observations has been given.

INTRODUCTION

The magneto-resistance change of ferromagnetics in an unidirectional field has been the subject-matter of investigation of various workers ; but as far as the author is aware very little work has been done relating to magneto-resistance change in alternating magnetic fields. Some recent workers ^{1,2} have shown that the passage of alternating current through a ferromagnetic wire alters to a considerable extent its electrical properties. This change in the electrical properties is a complex effect and may be partly due to the passage of alternating current as such through the material, partly of the nature of skin effect due to the permeability changes in the ferromagnetic caused by the alternating magnetic field of the alternating current and partly due to the alternating magnetic field itself. It is the purpose of this work to throw some light on the effects of an alternating magnetic field on the resistance of ferromagnetics as separated from the effect of passing an alternating current through the specimen and the consequent skin effect.

EXPERIMENTAL ARRANGEMENTS

It is known³ that the resistance of a ferromagnetic wire undergoes no change due to the passage of a direct current within moderate limits. For this reason, a constant direct current of the value of 0.1 Amps, as read by an ammeter placed in series with the specimen, was used for measuring the resistance of the wire, throughout the whole experiment. For measuring the resistance, the well known Kelvin's double bridge was used and with this arrangement, a resistance change of the order of 10 micro-ohms could be determined with accuracy, which was found enough for the purpose in view. The specimen in the form of a wire was placed longitudinally in the centre of a solenoid, the length of which was much greater than that of the wire, so that the full wire could be subjected to an uniform magnetic field. The solenoid consisted of two sections of wires wound one above the other, through one of which a direct current could be passed and through the other, an alternating current, and in this way, the specimen could be subjected either to a longitudinal direct magnetic field or to a longitudinal alternating magnetic field or to both simultaneously. Two specimens of wires were investigated. One was of pure nickel and the other was of Ni-iron permalloy of low coercivity. The coercivities of the two specimens were determined by the usual magnetometer method.

RESULTS

TABLE I.

Nickel.

Coercive field—7.80 Gauss. Length of the wire—57.5 cms. Diameter of the wire—0.048 cms. Resistance of the wire—0.336 ohms.

Alternating Longitudinal Field in Gauss.	Direct Longitudinal Field—Nil.	Direct Longitudinal Field—19.3 Gauss.		Direct Longitudinal Field—39.6 Gauss.	
	dR in Ohms $\times 10^{-4}$.	dR due to Alternating field alone in Ohms $\times 10^{-4}$.	Total dR in Ohms $\times 10^{-4}$.	dR due to Alternating field alone in Ohms $\times 10^{-4}$.	Total dR in Ohms $\times 10^{-4}$.
0	0	0	5.14	0	8.40
2.75	0	...	...	...	...
3.62	0	...	...	...	...
5.43	...	0	5.14	...	...
10.13	1.44	0	5.14	0	8.40
14.47	2.70	0	5.14	0	8.40
21.71	4.14	0	5.14	-0.36	8.04
28.04	5.76	1.08	6.22	-0.72	7.68
36.18	7.20	3.42	8.56	-0.54	7.86
51.27	11.52	6.84	11.98	1.56	9.96
72.37	14.04	10.16	15.30	4.68	13.08
90.45	16.56	12.70	17.84	6.48	14.88
108.54	19.62	16.20	21.34	9.18	17.58

TABLE II.
Ni-Iron Permalloy.
Coercive field—1.40 Gauss. Length of the wire—53.5 cms. Diameter of the wire—0.045 cms. Resistance of the wire—1.67 Ohms.

Alternating Longitudinal field in Gauss.	Direct Longitudinal field—4.88 Gauss.		Direct Longitudinal field—9.65 Gauss.		Direct Longitudinal field—19.5 Gauss.		Direct Longitudinal field—38.6 Gauss.	
	dR in Ohms $\times 10^{-4}$.	dR due to Alternating field alone in Ohms $\times 10^{-4}$.	Total dR in Ohms $\times 10^{-4}$.	dR due to Alternating field alone in Ohms $\times 10^{-4}$.	Total dR in Ohms $\times 10^{-4}$.	dR due to Alternating field alone in Ohms $\times 10^{-4}$.	Total dR in Ohms $\times 10^{-4}$.	
0	0	0	15.41	0	22.11	0	32.16	
1.26	0	...	...	...	...	...	...	
1.81	2.06	0	15.41	...	...	...	...	
2.71	3.69	0	...	...	...	...	...	
3.62	5.36	-1.01	...	...	22.11	...	...	
3.98	...	...	15.07	...	...	...	...	
4.52	...	-1.31	...	...	...	...	...	
5.13	7.37	0	14.74	0	22.11	...	...	
7.60	...	...	11.07	-1.34	20.77	...	32.16	
7.96	...	...	...	...	...	...	...	
10.49	13.40	6.70	...	...	...	...	...	
10.85	...	...	14.74	-0.67	...	...	...	
11.22	...	...	...	...	20.05	-1.37	30.79	
15.20	16.08	11.75	15.75	0.54	18.76	-3.35	...	
18.09	...	...	...	...	19.43	-2.68	...	
21.71	20.10	13.49	22.44	7.03	22.11	0	...	
25.33	...	16.75	...	...	...	...	28.81	
28.04	24.12	...	23.46	10.05	...	...	27.47	
32.06	...	...	...	...	...	...	25.79	
36.18	27.47	21.41	27.47	12.06	...	...	20.60	
43.42	...	...	...	...	...	...	28.81	
54.27	32.16	26.13	31.83	10.40	...	...	31.79	
72.37	36.85	27.81	36.85	21.14	9.72	1.31	33.17	
90.45	38.50	20.80	38.50	23.12	11.35	2.85	34.51	
108.54	38.50	20.80	40.57	25.46	13.20	5.22	37.18	
					15.70	6.37	38.53	

Tables I and II give the results obtained with nickel and Ni-iron permalloy, respectively. The second column in both the tables gives the resistance change of the specimens when subjected to only alternating magnetic field. The other columns represent the measurements taken with a simultaneous application of a direct and an alternating magnetic field. The results are best appreciated with reference to figures 1 and 2 which are graphical representations of the results obtained.

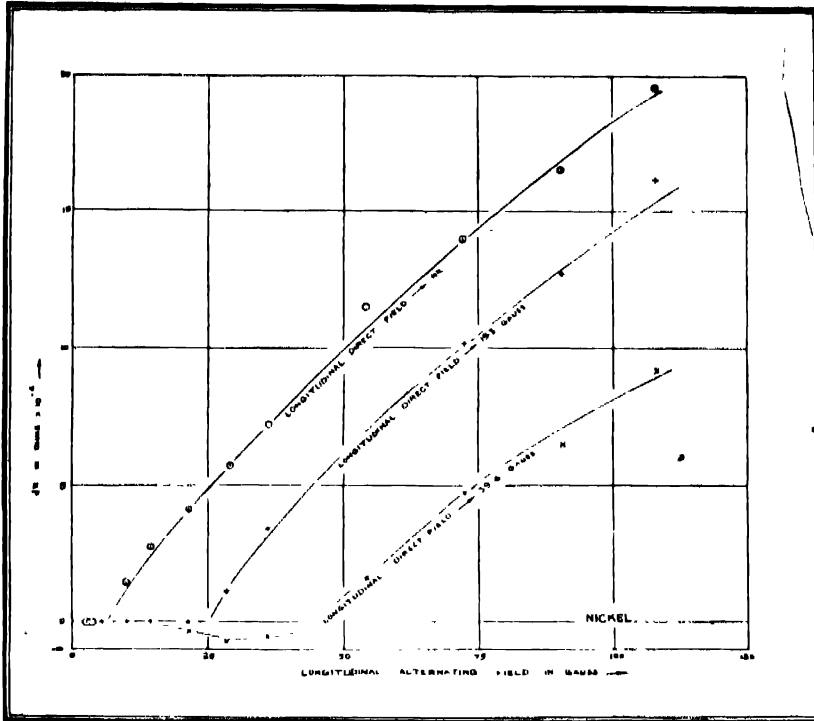


FIGURE 1.

It will be seen that when a ferromagnetic wire is subjected to a gradually increasing alternating magnetic field alone, the resistance of the wire undergoes no change in the beginning till a certain value of the alternating field is reached and then if the field be further increased, the resistance increases practically in the same way as it does under a direct magnetic field. The particular value of the alternating field after which the resistance begins to increase, which we shall call H_0 , agrees with the coercive field H_c of the specimen, as will appear from table III. The magnitude of the change of resistance with alternating field appears to be of the same order as that with a direct field as table IV shows. The smaller resistance change with alternating field merely points to the fact that a portion of the alternating field perhaps goes to overcome the coercive field of the specimen and hence the resistance changes in alternating field refer to smaller fields than

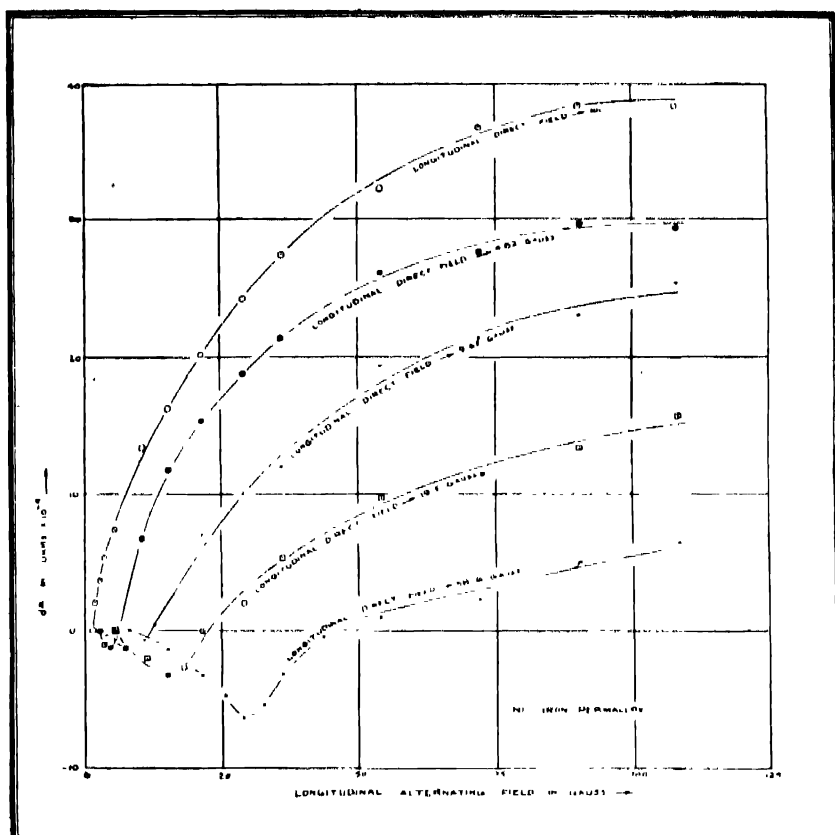


FIGURE 2.

the corresponding direct fields given in table IV. The tables III and IV are merely analysis of the data given in tables I and II and the curves of figures 1 and 2. So far concerning resistance change under the effect of alternating field alone.

Now let us consider the resistance change under a simultaneous effect of direct and alternating fields. When a direct field is at first applied, there is a consequent increase in the resistance of the specimen, as given in the tops of columns 4, 6, 8 and 10 of tables I and II. If now an alternating field be superimposed on the direct field, a decrease of resistance first takes place and then after reaching a minimum value, the resistance again increases, passing through the value it had at zero alternating field and finally reaches nearly the same values as it did under the effect of the alternating field alone. For the purpose of neatness and clarity no account is taken in figures 1 and 2 of the resistance change of the specimen due to the direct field, but this is taken into account in the columns 4, 6, 8 and 10 of tables I and II.

TABLE III.

Specimen.	H_0 in Gauss.	H_m in Gauss.	H_0/H_m .	H_o in Gauss.	H_c in Gauss.	$H_0 + H_c$ in Gauss.
Ni-Iron Permalloy	0	...	...	1.50	1.40	1.40
Do	4.82	4.00	1.21	6.00	1.40	6.82
Do	9.65	7.45	1.30	12.00	1.40	11.05
Do	19.50	15.00	1.30	21.50	1.40	20.90
Do	38.60	29.50	1.31	44.50	1.40	40.00
Nickel	0	..	...	6.50	7.80	7.80
Do.	19.30	...	...	25.00	7.80	27.10
Do.	39.60	30.00	1.32	44.50	7.80	47.40

TABLE IV.

Specimen.	Field value Alternating or Direct in Gauss.	dR in Alternating Field $\text{Ohms} \times 10^{-4}$.	dR in Direct Field $\text{Ohms} \times 10^{-4}$.
Ni-Iron Permalloy	4.82	6.30	5.36
Do.	9.65	12.00	15.41
Do.	19.50	19.50	22.11
Do.	38.60	29.00	32.16
Nickel	19.30	3.80	5.14
Do.	39.60	8.00	8.40

DISCUSSION OF THE RESULTS

If,
 H_m = the alternating field at which the resistance has a minimum value,
 H_d = the direct field,
 H_o = the alternating field after which the resistance finally begins to increase,
then two very remarkable results can be noticed from table III.

$$H_o = H_d + H_c \qquad \dots \quad (1)$$

$$H_d/H_m = 1.30 \text{ nearly} = \text{constant} \quad (2)$$

The relation (2) has a very significant meaning in the light of the following observations. The alternating field that is created by the passage of an alternating current through a solenoid is a fluctuating field passing through a maximum in one direction 50 times per second just like the current. Now as it is the root mean square value of the current which is read by an A.C. ammeter, it is the root mean square value of the alternating field that is obtained when calculated from the alternating current and not the maximum value. If it is supposed that the resistance is minimum when the maximum value of the alternating field is equal to the direct field, the relation $H_d/H_m = 1.30$, shows that the crest factor of the current used is 1.30 which is near the correct value.

The relation (1) again points to the fact that the direct field applied behaves just like the coercive field in this case and unless the alternating field is more than the sum of the coercive field and the direct field, no increase in resistance takes place.

Another important observation should be made in this connection. The magnitude of the maximum decrease in the resistance of a ferromagnetic wire due to the superimposition of an alternating field over a direct field increases with the value of the direct field applied.

The above remarkable observations are capable of being explained on the general theories of magneto-resistance change. It is known that there is always an increase of resistance, whatever be the direction of the magnetic field applied. The increase in resistance, therefore, in an altering magnetic field similar to that in a direct longitudinal field is quite expected, and is a sort of average of the varying resistance changes during a cycle. The fact that the resistance does not begin to increase until the coercive field is overcome by the alternating field has also a parallel in the case of the direct field if we consider a full resistance-hysteresis curve.

The effects of the superimposition of alternating and direct fields can be similarly explained. An alternating field helps the direct field during one half of the cycle and opposes it during the other half. There is an increase of resistance, therefore, in half the cycle when the two fields are helping each other and a decrease in the other half; but the increase of resistance is necessarily less than the decrease as is clear from the nature of the magneto-resistance curves. The net result therefore in a complete cycle is that there is a decrease of resistance. This goes on till the peak value of the alternating field equals the direct field and then the maximum decrease in the resistance takes place. It is clear that the maximum decrease in the resistance will be greater, the greater the value of the direct field applied. After this point is passed, an increase in the alternating field increases the resistance of the wire and the usual form of the magneto-resistance curve is obtained.

A part of this work was carried out in the Physics Laboratories of the Science College, Patna, and the author is thankful to the authorities for kind permission, and to Prof. K. Prosad, I.E.S., specially who has shown a very keen interest in this piece of work.

PHYSICS LABORATORY,
BILHAR COLLEGE OF ENGINEERING,
PATNA.

R E F E R E N C E S

- ¹ Harrison, Turney, Rowe, & Gollop, *Proc. Royal Soc.*, **47**, 451 (1936).
- ² Sen Gupta, Mohanti and Sharan, *Z. f. Phys*, **98**, 262 (1935).
- ³ Strierstadt, *Phys. Rev. (2)*, **37**, 1356 (1931)
- ⁴ Gerlach, *Proc. Phys. Soc.*, **42**, 418 (1930).

A STUDY OF THE F-REGION OF THE IONOSPHERE

By R. R. BAJPAI

AND

B. D. PANT.

Physics Department, Allahabad University.

(Communicated by Prof. M. N. SANA, F.R.S.)

(Received for publication, May 10, 1938)

ABSTRACT The results of ionization measurements in the F-region during Oct., Nov. and Dec., 1936, are reported. A number of typical curves showing the diurnal variation of electron density are given and their salient features discussed.

Separate existence of the F_1 -region has been observed till a few hours after sunset.

Evidence is summarized to show that solar theory of upper atmospheric ionization is inadequate to explain all the observed phenomena. Either the theory should be modified or some other source or mechanism of electron production should be found out.

1. INTRODUCTION.

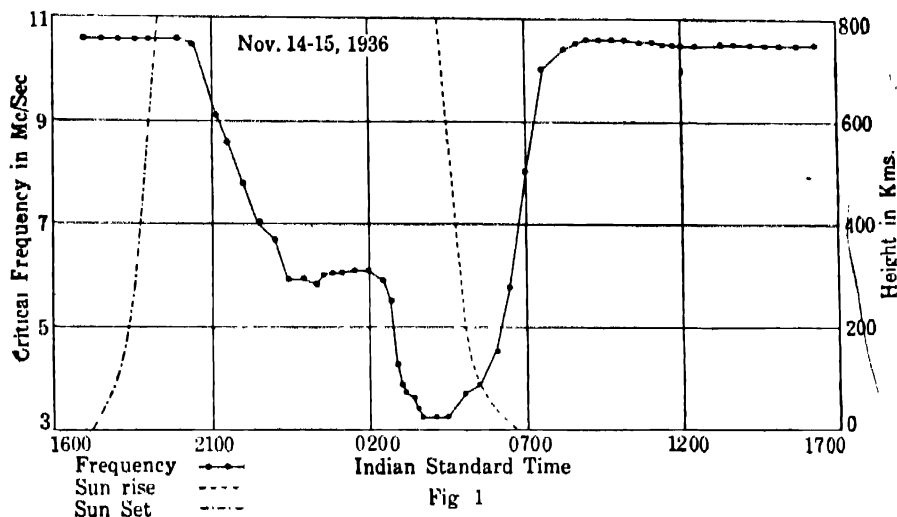
The paper presents the results of weekly measurements of ionization in the F-region at Allahabad (Lat. $25^{\circ}25'55''N$, Long. $81^{\circ}55'0''E$) during the months of October, November, and December, 1936. The observations were generally started on Saturday evenings and closed on Sunday evenings. A description of the apparatus along with some interesting results concerning a new condition of reflection discovered from the value of the difference between the critical penetration frequencies for the α - and x -waves is in the course of publication elsewhere. During most of the runs the critical penetration frequencies of F_2 -region and night F-region only were measured, however, on certain days we found the electron content of both the F_1 and F_2 regions.

2. EXPERIMENTAL RESULTS.

A. NOTES ON CURVES ILLUSTRATED

Considerable variations have been found in the ionization of the F_2 -region and in its diurnal behaviour from one period of observation to another. We shall now describe some of the typical critical penetration frequency curves showing the diurnal variation of the maximum electron density per c.c. in the F_2 -region.

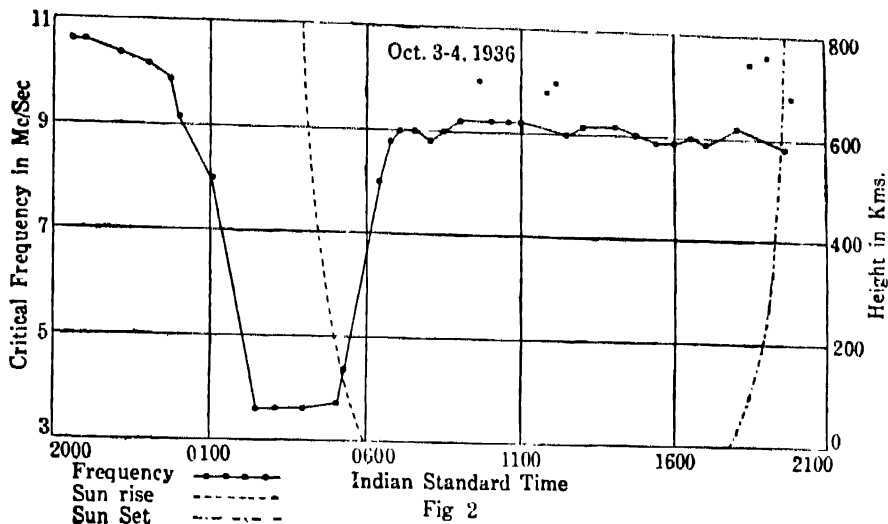
Fig. 1—November 14-15, 1936—represents a typical curve showing the diurnal variation in the critical penetration frequency of the F_2 -region during this part of the year. We observe that the critical penetration frequency



remains constant at 10.6 mc./sec. ($N=1.4 \times 10^6$) from 17.00 to 20.00 (I.S.T.). From a comparison of the sun set curve* it is seen that the ionization does not fall till an hour and a half after the sun has set in the region (at a height of 300 kms.). From 20.30 (I. S. T.) a rapid decrease in ionization is noticed, and the critical penetration frequency falls to a value of 5.9 mc./sec. at 23.30 (I. S. T.), whence the ionization begins to increase. We notice an imperceptible broad maximum at about 01.45 (I. S. T.). From 02.40 (I. S. T.) the ionization again commences to decrease rapidly and, at 03.30 (I. S. T.) the critical penetration frequency attains the minimum value of 3.2 mc./sec. which does not change till 04.30 (I. S. T.), when the ionization is seen to build up rapidly. The sun rise curve shows that the early morning increase in ionization begins about 20 minutes before sun-rise at a height of 300 kms. The rapid increase in ionization is seen to continue only up to 07.30 (I. S. T.), after which there is only a slow variation with a broad maximum at about 09.30 (I. S. T.) followed by a very shallow minimum at noon.

Fig. 2—October 3-4, 1936—We observe that on this curve, the night maximum in ionization, which is normally observed during this part of the year, is not to be seen. The ionization is seen to decrease, first slowly and then rather rapidly, there being a regular fall throughout. We notice that the critical penetration frequency is almost constant at 3.6 mc./sec. between the hours 02.30 and 05.00 (I. S. T.) The pre-sun-rise increase in ionization is also absent. On October 3,

* In drawing the sun-set and sun-rise curves the correction due to refraction has not been taken into account.



the critical penetration frequency is seen to have suddenly increased a number of times, as is shown by dots above the regular curve. Such increases in F_2 region have been observed at other places as well, and are probably due to sudden formation or arrival of dense patches of electrons. The occurrence of such local electronic clouds has been pointed out by other workers.¹ We observe, that the value of the critical penetration frequency on the evening of October 3, is about 1.5 mc./sec. higher than that on the following day.

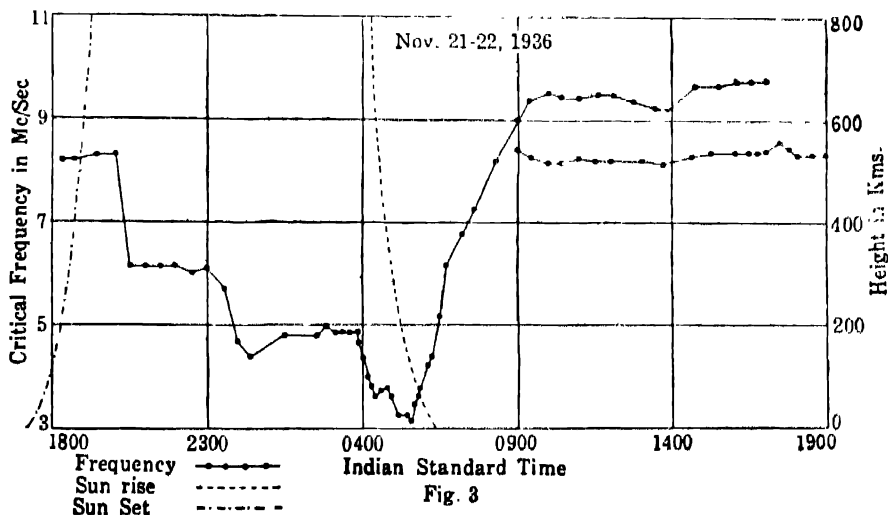


Fig. 3—November 21-22, 1936—One of the special features of the curve is that, instead of one, there are two secondary maxima (one very flat) of ionization during the night. We also notice that there is no pre-sun-rise increase in ionization but we observe that in the evening the ionization is not seen to fall till a little more than an hour after the sun has set in the region. The increase

in ionization on the morning of 22nd November is seen to begin actually 20 minutes after sun-rise at the height of the F region. From 09.00 (I. S. T.), it is found that the F-region splits up into F_1 and F_2 .

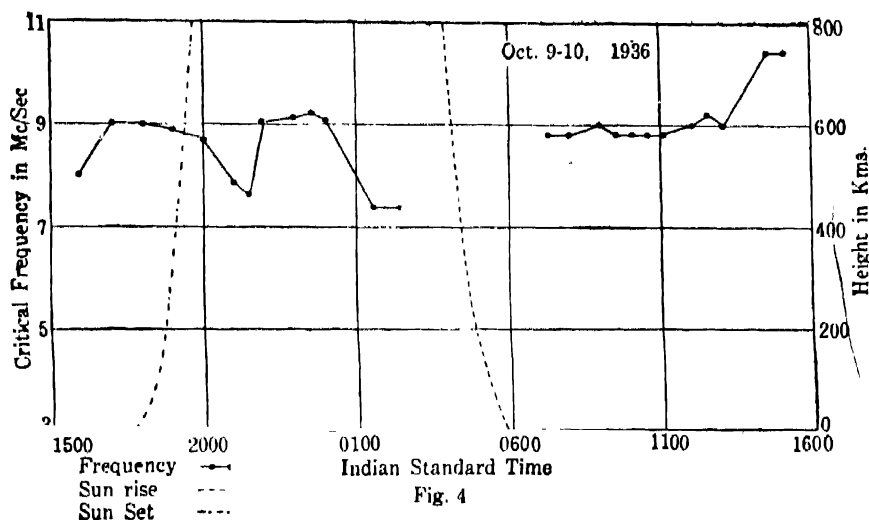
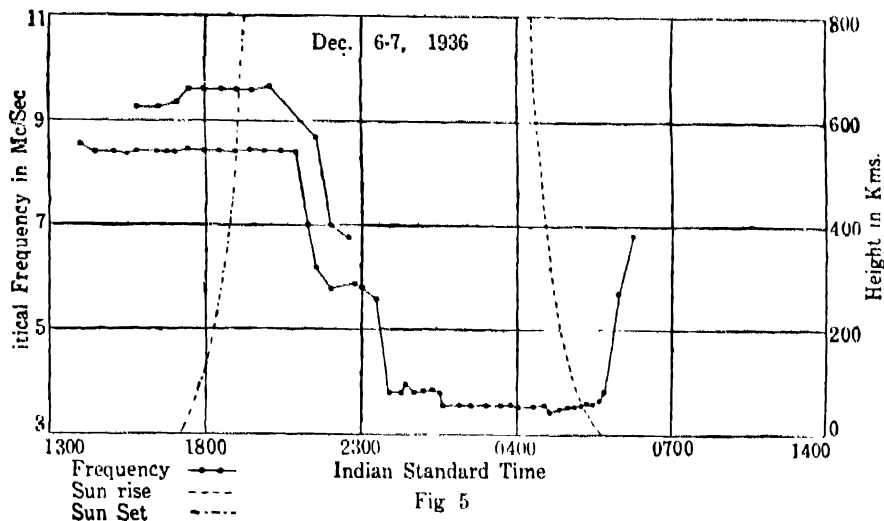


Fig. 4—October 9-10, 1936—It appears to us that the ionosphere was much disturbed on these dates. The report* from the Colaba observatory, Bombay on the magnetic character of each day describes these days as those of small disturbance, but we suspect that there was some local magnetic disturbance also, for on other days described as of small disturbance in the above report we do not notice any such peculiarities. We observe a broad maximum in the evening centered between the hours 17.00 and 18.00 (I. S. T.), after which there is slow but regular fall in ionization. At 21.30 (I. S. T.) a sharp minimum is to be noticed, whereafter a sudden increase in ionization is observed. It is to be noticed that at 21.30 (I. S. T.) the critical penetration frequency becomes 9.2 mc./sec., a value higher than that in the evening hours. After mid-night a regular decrease is seen to take place which continues for about an hour and a half. The critical penetration frequency remains constant between the hours 01.30 and 02.30 (I. S. T.). Observations could not be taken between 02.45 and 07.15 (I. S. T.) due to failure of power supply. A sudden increase in ionization on the 10th evening is to be noticed.

Fig. 5—December 6-7, 1936—On this day the ionization of both, the F_1 and the F_2 regions, was measured. We observed separate existence of both the regions till about 10 o'clock at night. The ionization is seen to remain constant

* We are indebted to Dr. C. W. B. Normand, Director-General, Meteorological Department of the Government of India and to Dr. K. R. Ramanathan, Meteorologist-in-charge of the Colaba Observatory, for the regular supply of these reports.



for a period of a little over two hours after sun-set. This night existence of the F-region has not been reported by any European or American worker who report that it is only a day-light phenomenon. However, Bhar² at Calcutta, has reported the existence of both the regions throughout the night during November, 1936.

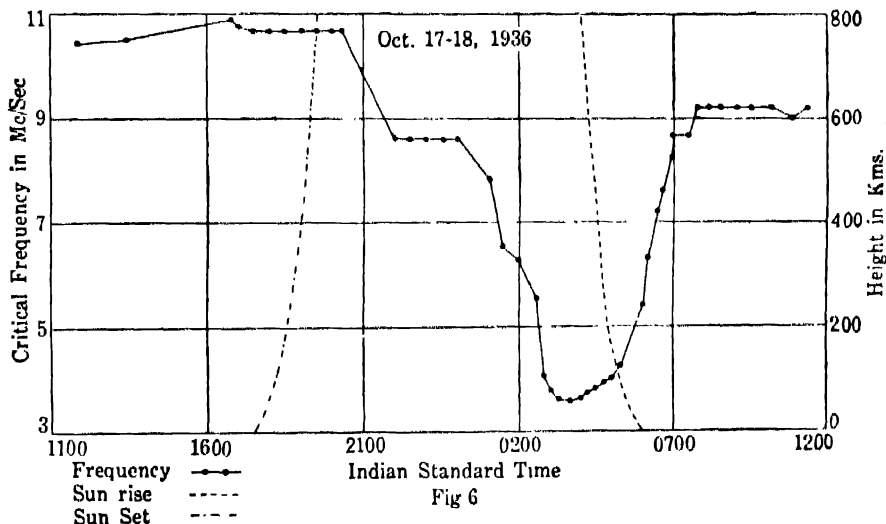


Fig. 6—October 17-18, 1936—The general features of the curve are similar to those of figure 1. We observe an evening maximum at about 16.45 (I. S. T.) and, instead of a secondary night maximum, the critical penetration frequency remains constant at 8.6 mc./sec. between the hours 22.00 and 24.00 (I. S. T.). On this date also we notice that the ionization does not begin to fall till about an hour and a half after the sun has set in the F₂-region.

B. RECOMBINATION COEFFICIENT

If we assume that electrons are only lost by recombination with positive ions and that the number of electrons is equal to the number of positive ions, we can write for day time conditions that

$$\frac{dn}{dt} = q - \alpha N^2 \quad \dots (1)$$

where, q = number of electrons produced per c. c. per sec.

α = recombination coefficient.

N = number of electrons per c. c.

For night time conditions we have

$$\frac{dn}{dt} = -\alpha N^2 \quad \dots (2)$$

which on integration yields

$$\frac{1}{N_2} - \frac{1}{N_1} = \alpha(t_2 - t_1) \quad \dots (3)$$

where, N_1 = Number of electrons per c.c. at time t_1 ,

N_2 = number of electrons per c. c. at time t_2 .

The following table gives the value of α as observed on a number of nights.

TABLE I.

Date.	$\alpha \times 10^{10}$.
3.10.36	3.9
17.10.36	5.5
7.11.36	8.0
14.11.36	3.2
21.11.36	7.9
28.11.36	7.3
6.12.36	3.7

3. DISCUSSION OF RESULTS.

A. THE DIURNAL VARIATION OF ELECTRON DENSITY.

In discussing the diurnal variation of the electron density in the F₂-region we shall chiefly confine ourselves to the typical curve given in figure 1. We observe that the minimum of ionization is reached at 03.40 and a steady value of 1.5×10^5 electrons per c. c. continues for about an hour, whence there is a sharp rise. It is obvious from the sun-rise curve that at the time of this sharp increase, there are still 20 minutes before the sun will rise at a height of 300 kms. However, we can roughly say that with the incidence of the rays of the sun in the region the ionization begins to build up rapidly, probably through the process of photoionization. As the sun's zenith angle decreases, the rate of increase in ionization is seen to increase up to about 07.00 when it begins to decrease. Thus it is seen that, although the sun's zenith angle is decreasing and the rays responsible for ionization are reaching the region with greater intensity, yet the rate of increase of free electrons is decreasing.* The law that ionization should vary as $\cos^{\frac{1}{2}}\chi$ as the solar theory demands, is flagrantly contradicted. We think that at this time the electrons begin to attach themselves to heavier particles. Most probably oxygen molecules get dissociated and a large number of oxygen atoms are formed. As atomic oxygen has got a great affinity towards free electrons (according to Smythe's measurements, it is 2.2 volts), the latter get attached and are thus rendered ineffective so far as the reflection of radio waves is concerned. With the increase in the altitude of the sun, greater number of oxygen atoms are produced. This enhances the rate of attachment of electrons. Thus we obtain that although the rate of production of electrons is increasing, yet the rate of increase in the number of free electrons is seen to decrease. At about 09.00 the rate of formation of ions becomes equal to the rate of disappearance of electrons through attachment and recombination. At midday the number of electrons lost by attachment and recombination becomes greater than those produced and we observe a dip in the equilibrium value of free electrons. In the evening upto about 2 hours after sun-set the attached electrons get detached† and oxygen atoms recombine to form O₂ at such a rate that the equilibrium value of electron density is main-

* It may be pointed out here that it is not necessary that the equilibrium value of the electron density must go on increasing with the altitude of the sun, having a maximum at noon, for what is obtained from Chapman's¹ theory is the rate of production of ions and not the equilibrium value as obtained by experiments. The two will be proportional to each other only if the number of electrons is equal to the number of positive ions. It cannot be said that the proportionality will hold even in the presence of a host of other particles like O₂, O₂⁺, O₂⁻, O⁺ and O⁻ which are necessarily present during the day.

† The necessity of detachment of electrons at night was first suggested by Martyn and Pulley⁴.

tained almost at the same value. Among other subsidiary processes helping to maintain the maximum number of electrons per c. c. constant may be contraction due to cooling and helio-centric winds.⁵ After about 8 o'clock at night the equilibrium value of electron density begins to fall; probably by this time the number of O^+ decreases sufficiently so that detachment along with other processes at work is unable to maintain the same value of electron density and the electrons get lost through recombination.

B. INCREASE IN ELECTRON DENSITY AT NIGHT.

It is clear from figure 1 that the electron density in F-region after falling by a considerable amount, becomes almost steady at 23.30 (I. S. T.), and retains the steady value till 02.30 (I. S. T.), when it begins to fall again. The existence of this night phenomenon in F region ionization was first noted at the Bureau of Standards, Washington, during the last sun spot minimum and, at that time, it was found that during these hours, there was even some increase in electron density.⁶ Gilliland, Kirby, Smith and Reymer,⁷ however report that this post-midnight increase of ionisation has been found to dwindle with the approach of sun spot maximum. It is apparent from the ionization measurements of the above-named authors and those of Appleton and Naismith⁸ that this phenomenon occurs during winter nights only.

We observe that no satisfactory explanation has so far, been put forward to account for the behaviour of the ionisation curve during these post-midnight hours. As this part of the sky is not illuminated during these hours, the electron density ought to continue to fall rapidly, but we find that the curve is nearly horizontal, nay at times the ionisation increases. Martyn and Pulley⁴ made an attempt to explain these features. They observed that a correlation existed between the percentage increase in maximum electron density and in the virtual height, which diminished. From these facts, these authors conclude that the increase in electron density during these hours is due to the contraction of the region as a whole due to night time cooling; but a critical examination of their reasoning shows that the argument is rather crude, for the region of maximum electron density constitutes only a small part of the total contracting region and we cannot extrapolate this density over the whole ionosphere as Martyn and Pulley have done. Further their assumption that the lower limit of contracting region is 80 kms, appears to be rather arbitrary*. There may be further very large difference in temperature between 80 and 250 kms, hence one is not justified in talking of average contraction. Again the apparent decrease in virtual height may be all illusory, because what we measure is the group-time. The actual height is the time-interval observed multiplied by the

* See Hulburt⁵ who thinks that contraction does not extend below F₁-layer.

group-velocity. Now this velocity decreases, as the curves of Bajpai and Mathur⁹ show, with increasing electron-concentration. So as night proceeds, the group-velocity in the lower regions goes on increasing. Hence the actual height in the post-midnight hours may be quite as large as at about midnight. Further, it may be asked that if the increase in electron density is simply due to contraction of the region, why it does not start for a number of hours after sun set, why it comes to a stop several hours before sun-rise, and why the phenomenon is not observed at all on summer nights. It appears therefore that the phenomena involved are too complex, and the solar theory of ionisation is not adequate for explaining all the observed facts.

It is expected that if night time ionisation data are available from a number of places widely different in latitudes situated in both the hemispheres, it may be possible to understand the problem.

C. INADEQUACY OF THE SUNLIGHT THEORY.

This view is further supported by the valuable observations on the diurnal and seasonal variations of the F_2 -region ionization which show similar characteristics at several widely different latitudes, north and south, at the same time of the year¹⁰ while from a solar theory we would expect that the corresponding changes would be seasonal. The results of the radio observations of the British Expedition at Tromsø during the Second Polar year, 1932-33, brought to light another fact that at Tromsø the F_2 -region critical penetration frequency was found to be greater at mid-night (when the sun was only 1° above the horizon) than that at midday (when the sun was 45° above the horizon) at the time of the mid-night sun.¹¹ It flagrantly contradicts the solar theory, for if ionization is simply due to the ultraviolet light of the sun the effect would be the reverse.

Very recently ionospheric investigations carried out by an Oxford University expedition¹² to North-East Land (Lat. $80^\circ 23' N.$, Long. $19^\circ 31' E.$) have brought forth further facts having an important bearing upon this problem. They find that abnormal E-region exists throughout the four and a half months of the dark period at North-East Land without any discontinuity in the critical penetration frequency curves at the time when the earth's shadow reaches the E-layer at noon or at any other time. It appears that the ionization in this E-region is maintained here by electrons from the sun which, on account of the focussing action of the earth's magnetic field round the magnetic pole, continue to reach these places even during the dark period. Another possibility also exists that electrons produced by the ultraviolet light of the sun at lower latitudes are carried over to these dark regions on account of the magnetic field of the earth. It is, however, remarkable to note that this E-region continues throughout winter at North-East Land but is completely absent at Tromsø during this season of the

year, although both these places are almost similarly situated as regards the North magnetic pole.

A comparison of the critical penetration frequency curves for Tromsø and North-East Land shows that the F_1 -region, after the disappearance in winter, reappears six weeks earlier at North-East Land than at Tromsø. In view of the respective situations of the two places, this is against the expectations from the sun-light theory. Thus the evidence is accumulating which shows that the sun light theory of upper atmospheric ionization is unable to explain a number of phenomena concerning the upper atmospheric ionization. Either the theory should be modified or some other forces at work which are responsible for these phenomena should be found out. We may also look for some other source or mechanism of ion production which may satisfactorily explain all these facts.

D. DECREASE OF IONIZATION IN THE SMALL HOURS OF THE MORNING.

Figure 1 and the curves given by Gilliland⁶ and Gilliland, Kirby, Smith and Reymer⁷ clearly indicate that after the night maximum in ionization, there occurs a sudden decrease in the electron density of the F -region in the pre-dawn hours.

Hulburt⁵ suggested that the disturbed condition of the layer in the morning is due to helio-centric winds. Martyn and Pulley⁴ ascribe this decrease of ionization in the early morning to the inrush of air due to these winds. There is, however, a serious difficulty in the way of this explanation. According to this view we should get this sudden decrease in ionization in the small hours of the morning throughout the year, but Gilliland⁶ and Gilliland, Kirby, Smith and Reymer's⁷ work shows that the decrease in ionization on a summer night is quite regular, there being no change in the rate of decrease in the small hours of the morning. There appears to be no reason as to why the helio centric winds should not blow during the summer months. It appears to us that this decrease does not constitute a problem in itself. As soon as a satisfactory explanation of the increase in ionization during post midnight hours is found the question of this morning decrease does not arise, for when the unknown source that increases the maximum electron density becomes inactive, the ionization is bound to fall.

E. MINIMUM IONIZATION AND THE TIME OF SUN-RISE IN THE F_2 -REGION.

Figure 1 shows that the ionization begins to increase about 20 minutes before the sun rises at a height of 300 kms, while figures 2 and 3 show that this increase

begins 20 minutes after the sun has risen at a height of 300 kms. Again figure 5 indicates that the increase in ionization in the early morning is delayed still further. It actually begins to increase one and a half hours after sun-rise in the F_2 -region. Thus it appears that, at least in the case of F_2 -region, there is no simple correlation between the time of sun-rise and the time of increase in ionization in the early morning and that there are some other factors to be taken into account. For such a correlation more data extending over a much longer period are required. However, at the suggestion of Prof. Saha it has been attempted in this laboratory.^{1,3} Data for Allahabad,⁴ Washington⁶ and Slough⁵ have been taken into consideration but correction due to refraction has not been taken into consideration. The general conclusion arrived at is that the height at which sun-rise takes place at the time of minimum ionization is greater during winter than that during summer in all latitudes, that in higher latitudes the F-region ionization begins to build up always after sun-rise in the region and that for the lower latitudes a rough statement has been made, and that during summer the ionization begins to build up after sun-rise in the region, while during winter it begins to do so before sun-rise. Chapman's^{2,3} theory of absorption of monochromatic radiation shows that the height at which the rate of ionization is maximum is greater during winter than that during summer. It may be due to this fact that in winter the height at which sun-rise takes place at the time of minimum ionization (in other words the time when ionization begins to increase) is greater than that in summer.

F. THE EXISTENCE OF F_2 -REGION AT NIGHT.

An important fact brought to light by this study is the separate existence of F_1 - and F_2 -regions during the early part of the night. Figure 5 clearly indicates that the two layers coalesce at about 22.30, *i.e.*, after a period of about five hours after ground sun-set. On the other hand American and English workers report that the two layers merge into each other near about ground sun-set. However, Blar's² ionization measurements at Calcutta indicate the separate existence of both these layers throughout night. It is remarkable that Gilliland, Kirby, Smith and Reymer⁷ report that during 1936 winter, they were not able to observe any F_1 layer even during the day.

G. RECOMBINATION COEFFICIENT.

The observed value of the recombination coefficient has been found to vary from 3.2×10^{-10} to 8×10^{-10} from one period of observation to another as is shown in table 1. It may be mentioned that the values of α have been calculated on the assumption that the number of electrons is equal to the number of positive

* See also Appleton¹⁴

ions which is not correct,* for electrons get attached to neutral particles as well. Thus we see that the relevant equation for equilibrium during day time should be

$$\frac{dN}{dt} = q - \alpha N_e (N^- + N_e) \quad (4)$$

where N_e = Number of electrons per c. c.

N^- = Number of negative ions per c. c.

and for night time conditions we have

$$\frac{dN}{dt} = -\alpha N_e (N^- + N_e) \quad (5)$$

It is clear from (5) that the value of α calculated from (5) will be smaller than that calculated from (3), depending upon the value of N^- . Saha and Rai, in some unpublished work of theirs, have theoretically calculated the value of α to be 1.25×10^{-11} . This value will be in excellent agreement with our observations if the correction due to the presence of N^- is taken into consideration.

Our grateful thanks are due to Prof. M. N. Saha, D.Sc., F.R.S., for his kindness on the authors in granting them scholarships out of his personal research grant from the Government of the United Provinces and for many useful discussions and suggestions regarding the presentation of the paper.

We also wish to record our best thanks to Dr. G. R. Toshniwal for his keen interest and suggestions.

We are also thankful to Mr. K. B. Mathur, M.Sc., for help in taking some observations.

REFERENCES.

- ¹ Schafer and Goodall, *Proc. Fifth Pacific Sc. Congress*, **3**, 2171 (1924).
- ² Bhar, *Ind. Jour. Phys.*, **11**, 109 (1937).
- ³ Chapman, *Proc. Phys. Sc.*, **43**, 26 (1931).
- ⁴ Martyn and Pulley, *Proc. Roy. Soc. A*, **154**, 755 (1936).
- ⁵ Hulburt, *Terr. Mag.*, **40**, 143 (1935).
- ⁶ Gilliland, *Proc. Inst. Rad. Eng.*, **23**, 1076 (1935).
- ⁷ Gilliland, Kirby, Smith and Reymers, *Proc. Inst. Rad. Eng.*, **25**, 823 (1937).
- ⁸ Appleton and Naismith, *Proc. Roy. Soc. A*, **150**, 685 (1936).
- ⁹ Bajpai and Mathur, *Ind. Jour. Phys.*, **11**, 165 (1937).
- ¹⁰ Berkner, Wells and Seaton, *Terr. Mag.*, **41**, 173 (1936).
- ¹¹ Appleton, Naismith and Ingram, *Phil. Trans. Roy. Soc. A*, **236**, 191 (1937).
- ¹² Whatman and Hamilton, *Proc. Phys. Soc.*, **50**, 217 (1938).
- ¹³ Mathur, *Proc. Nat. Acad. Sc. India* (In press).
- ¹⁴ Appleton, *Proc. Roy. Soc. A*, **162**, 685 (1937).
- ¹⁵ Massey, *Proc. Roy. Soc. A*, **163**, 542 (1937).

* See, however, Massey¹⁵ who thinks that in the F-region the number of positive ions is equal to the number of electrons,

HEXACOORDINATION IN TELLURIC ACID, AND IN MOLYBDATES AND TUNGSTATES IN SOLUTION

By JAGANNATH GUPTA.

(Received for publication, June 1, 1938)

Plate VI.

ABSTRACT. Following a previous communication on the subject, telluric acid and several molybdates and tungstates have been examined by their Raman spectra in the crystalline state and in aqueous solutions of definite hydrogen ion concentration. Theoretical and experimental evidences for the author's previous suggestion that in aqueous solutions, the normal molybdate and tungstate ions are present, like telluric acid, as dihydrated octahedral units, have been adduced. Extra lines recorded by other workers in solutions have been shown to be not due to vibrations of the normal molybdate or tungstate ions, but some of them are due to isopoly complexes present in such solutions.

INTRODUCTION.

Several oxyacids and their salts of the sixth group elements of Mendeleef's periodic table have been studied from time to time by their Raman spectra for the elucidation of their structures in the pure state and in aqueous solutions of different concentrations. The sulphate¹ and selenate² ions have been shown to be tetrahedral, and assuming the equivalence of the four bonds, the spectra have been interpreted and force constants for the S-O and Se-O bonds have been calculated.²

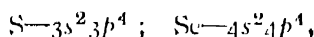
It was shown by the present author, however, that with telluric acid, the vibration spectrum showed important differences from the earlier members, both in the solid state and in solution, and could be satisfactorily interpreted by assuming an octahedral configuration of six oxygen atoms round Te^{vi} , two oxygen atoms other than the four atoms of the anhydrous acid coming from two molecules of water of crystallisation.³ Similar spectra were obtained for aqueous solutions of several normal molybdates and tungstates, on which the suggestion was made⁴ that in the aqueous solution the MoO_4^{2-} and WO_4^{2-} ions might each have been associated with two molecules

of water, the dihydrates remaining as octahedral units in solution. The following arguments may be put forward in support of this view :—

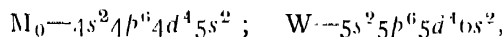
(1) Solid hydrates can often be isolated ⁵ (which may or may not possess the same elements of ionic symmetry as in solution¹).

(2) Hexavalent molybdenum and tungsten are predominantly 6-coordinating.⁶ The two elements have a tendency to exhibit high values for coordination number ⁷ in lower valence states.

(3) The electronic arrangement ⁸ of the outermost shell of sulphur and selenium, viz.,



where, after the acceptance of two electrons from the cation, the shells can easily form four bonds involving sp^3 eigenfunctions, are different from that of molybdenum and tungsten, viz.,



which, again, are very similar among themselves.

(4) In transitional elements, among which molybdenum and tungsten are two typical as shown in their many varying valence compounds, the d levels are vacant, with energies comparable with s and p levels. It is thus probable that under influences of the surrounding electric field caused by the H_2O dipoles, the quantisations involving $s-p$ combination may be broken and $s-p-d$ combinations may be formed. The octahedral structure is preferred when the bonds are appreciably ionic, and for large atoms surrounding the nuclear atom (oxygen is one of the 'large' atoms).⁹

(5) Instances are known ¹⁰ where the same central atom exhibits, in the 4-covalent state, a tetrahedral, and in the 6-covalent state, an octahedral arrangement of the coordinating groups, and where the conversion of a 4-covalent central atom to the corresponding 6-covalent state does not involve any drastic chemical treatment.

Recently, Venkateswaran ¹¹ has published a paper in which he claims to have recorded one extra line of zero intensity in each of the spectrograms of aqueous solutions of sodium molybdate and tungstate, and on the basis of the four lines present in his spectrograms, has concluded that these ions are simply tetrahedral in aqueous solutions. He has also criticised the present author's suggestion of octahedral unit formation as follows:—

(1) The spectra recorded by the present author were incomplete.

(2) Such evidences of hexacoordination are not obtained from a study of the Raman spectra of ammonium molybdate crystals.

(3) The force constants calculated on the basis of octahedral structure are not of the proper magnitude.

(4) $\nu_1^2 - (\nu_2^2 + \frac{3}{2}\nu_3^2) \neq 0$, as the present author assumed for vibrations of an octahedral molecule, but equal to $\frac{6(k' + k'')}{4l^2\pi^2c^2m_e}$, from Nagendranath's treatment,¹⁴ so that the equality $\nu_1^2 = \nu_2^2 + \frac{3}{2}\nu_3^2$ "went rather to disprove the possibility of any such structure for these ions."

In view of such differences of opinion, and of the experimental results obtained, most of the experimental work of the present author has since been repeated, and the results which have been described and discussed in the present paper along with Venkateswaran's, go to show definitely that the extra lines recorded do not belong to vibrations of the normal molybdate and tungstate ions.

EXPERIMENTAL.

Ammonium molybdate—The normal molybdate was freshly obtained by crystallising Merck's extra pure 'ammonium molybdate' from concentrated ammonia. Solutions of $pH = 9$ and $pH \gg 9$ were prepared by passing requisite quantities of ammonia gas into freshly prepared solutions of this salt in double distilled water. The solutions were quickly filtered into a Wood's tube which was then tightly closed with a rubber stopper to prevent escape of ammonia.

Ammonium paramolybdate—A solution of the paramolybdate was prepared by dissolving Kahlbaum's extra pure 'ammonium molybdate' (which is really the paramolybdate) in water and ageing the solution for 24 hours in a non-stoppered conical flask to allow escape of any excess of ammonia. The solution was filtered into a Wood's tube with usual care.

The crystals of ammonium paramolybdate, less accurately termed 'ammonium molybdate' by previous workers, were examined in the crystalline state using a blue uviol filter in the incident light from a quartz mercury arc lamp, and a solution of azoxybenzene in benzene of suitable concentration to just cut off the 4358Å group of lines in the scattered radiation.

Sodium and potassium molybdates—These were prepared by dissolving Merck's extra pure molybdic acid in chemically pure sodium and potassium hydroxides respectively, the bases being added in slight excess of the equivalent amount to keep the solution alkaline. The salts were crystallised by evaporation and redissolved in freshly prepared dilute alkalis.

Sodium and potassium tungstates—Kahlbaum's tungstic acid was digested with conc. HCl and washed with water (to remove small quantities of molybdic acid, traces of iron, etc.). It was dissolved in chemically pure alkali and reprecipitated with chemically pure conc. HCl. The precipitated acid, after thorough washing, was dissolved in slightly more than its equivalent amounts of sodium and potassium hydroxides respectively to keep the solutions during crystallisation distinctly alkaline in which only the normal molybdates and tungstates are stable.

Determinations of pH values were made with a Wulff Folien-Kolorimeter (accuracy ± 0.2). Where accurate determinations were unnecessary (e.g., in strongly alkaline solutions), the alkalinity of the solution was tested with phenolphthalein, each time before and after exposure.

Telluric acid—Tellurium, obtained by reducing tellurous acid with sodium sulphite and hydrochloric acid, was oxidised by chloric acid.¹² The solution on crystallisation first yielded less soluble products, and finally large transparent crystals of the orthoacid $H_2TeO_4, 2H_2O$. Both aqueous solutions and crystals were examined, the latter by the use of complementary filters described above.

The results are tabulated below, along with Venkateswaran's. Some of the spectrograms are reproduced in plate VI, along with Venkateswaran's for comparison, the latter being kindly sent to the present author and permitted to be published.

TABLE I.

Telluric acid.

Author.	Substance	Raman lines in cm^{-1}
C. S. V.	$H_2TeO_4, 2H_2O$ crystals	365 (2), 657 (0), 670 (10), 3121 (ob)
J. G.	Do.	* , 630 (1), 655 (6), 3050 + (2b)
Do.	Aqueous solution	345 (3b), 619 (1), 644 (10)
C. S. V.	20% aq. solution	357 (3b), 624 (1b), 647 (10)

* Absorption of complementary filter extends to this region.

† From separate spectrogram, photographed with iodine and sodium nitrite filters.

(1)		Ammon. paramolybdate soln.
(2)		(NH_4) ₂ MoO ₄ soln. (C. S. V.),
(3)		Normal ammon. molybdate soln.
(4)		Pot. molybdate soln. (alkaline)
(5)		Na ₂ MoO ₄ soln. (C. S. V.),
(6)		Sod. molybdate soln. (alkaline)
(7)		Ammon. molybdate soln. (ammoniacal)
(8)		Na ₂ WO ₄ soln. (C. S. V.),
(9)		Sod. tungstate soln. (alkaline)
(10)		Pot. tungstate soln. (alkaline)
(11)		Telluric acid soln.
(12)		Ammon. sulphate soln. (ammoniacal)

Raman Spectra

TABLE II.
Molybdates and Tungstates.

Author.	Substance.	Raman lines in cm^{-1} .
J. G.	Ammonium paramolybdate crystals	223 (2), 362 (1), 881 (4), 927 (7).
Do	Do, aqueous solution, $p_H = 5.8$	222 (3) 365 (2), 895 (5), 942 (10) D D D P
C. S. V.	$\text{NH}_4)_2\text{MoO}_4$ solution	218 (3), 367 (2b), 890 (4b), 944 (10)
J. G.	Normal ammon. molybdate solution, $p_H = 9$ $p_H > 9$ }	326 (6), 820 (4), 895 (10).
Do	Normal sodium molybdate solution, $p_H > 9$	320 (8), 823 (4), 891 (10)
Do	Normal potass. molybdate solution, $p_H = 9$ $p_H > 9$ }	319 (8), 823 (4), 891 (10) D D P
C. S. V.	Na_2MoO_4 solution	241 (6), 317 (4b), 841 (2b), 897 (8).
J. G.	Normal sodium tungstate solution, $p_H = 9.0$ $p_H > 9$ }	320 (6), 834 (4), 929 (10)
Do	Normal potass. tungstate solution, $p_H = 9.0$ $p_H > 9$ }	320 (3), 835 (1), 928 (5).
C. S. V.	Na_2WO_4 , 40% solution	325 (4b), 452 (6), 840 (2), 934 (10).

C. S. V.—Venkateswaran.¹¹

J. G.—present author.

Figures in parantheses indicate relative intensities, estimated visually. P—polarised D—Completely depolarised.

DISCUSSION OF RESULTS.

The structure of telluric acid has been recently discussed by Venkateswaran,¹¹ and since the views expressed therein agree in general with those of the present author, any further discussion is omitted. Accepting the ortho form of the acid, viz., $\text{Te}(\text{OH})_6$, the force constant $\text{Te}-\text{O}$ comes out with the help of Bright Wilson's approximate frequency formulæ¹³ as $k_{01} = 3.96 \times 10^5$ dynes per cm. The value does not differ greatly from one obtained by Venkateswaran from Nagendranath's equations¹⁴ (3.54×10^5).

It may, however, be seen from the table, as also from the spectrograms reproduced, that Venkateswaran's $(\text{NH}_4)_2 \text{MoO}_4$ solution gives a spectrogram identical with that of ammonium paramolybdate whose anion was formulated by Rosenheim as $[\text{H}_2 (\tilde{\text{MoO}}_4)_6]^{10-}$, where tetrahedral MoO_4 groups may be present on the basis of such a formulation.¹⁵ Aqueous solutions having p_{H} values equal to and greater than 9, where all iso-poly complexes are unstable and the normal molybdate ion is the only existing ion in solution,¹⁶ the spectrogram shows definite differences and contains three lines instead of four.

The number of lines recorded with potassium and sodium molybdate solutions of p_{H} equal to or greater than 9, is in each case three, and as is to be expected, have similar relative intensities and nearly identical values with those for normal ammonium molybdate solutions. It is to be noted that there is no fourth line in the spectrograms, although these are recorded with much greater intensities than was done by Venkateswaran (see plate).

The normal tungstate solutions yield similar results with three lines in the spectrograms having intensity relations absolutely similar to the three lines for molybdates. The spectrogram of sodium tungstate is more intensely recorded than Venkateswaran's, as the intensity of the line 834 will show, but $\Delta\nu$ 452 is not observed (see plate) in the present author's spectrogram.

It is therefore pertinent at this point to examine the arguments put forward by Venkateswaran to deduce tetrahedral structures of these ions in aqueous solutions. His evidences appear to the present author to be open to the following objections :—

1. The fundamental frequencies for MoO_4^- taken from the data for ammonium molybdate, are not the frequencies of the normal ion, because simple molybdate ions do not exist in aqueous solutions of the paramolybdate.¹⁷ The crystals of ammonium molybdate, so called, have a complex composition, and are not simply dihydrate of ammonium molybdate.

2. The four frequencies of molybdate and tungstate ions (only data for alkali salts have been taken which are less liable to form complexes) do not agree in general characteristics, e.g.,

$$\begin{array}{l} \nu_4 \left\{ \begin{array}{l} \text{MoO}_4^- = 317 \text{ (4)} \\ \text{WO}_4^- = 452 \text{ (9)} \end{array} \right. \quad \nu_2 \left\{ \begin{array}{l} \text{MoO}_4^- = 241 \text{ (0)} \\ \text{WO}_4^- = 325 \text{ (4)}, \end{array} \right. \end{array}$$

the figures in parantheses indicating intensities of the lines, as given by Venkateswaran. It appears unlikely that the molybdate and tungstate tetrahedra, considering the parallelism of these two elements in physical and chemical properties of their compounds,¹⁸ should possess such different structures as would involve so different changes in polarisability during the same mode of vibration. Results of X-ray analysis do not indicate such differences.

3. The four Raman frequencies of a tetrahedron are of comparable intensities, since all the modes are allowed in Raman effect, as data for all accepted tetrahedral molecules will show. The spectrogram of the sulphate ion, which is tetrahedral, is reproduced on the plate for comparison and the sharp difference is immediately apparent. The four lines recorded by Venkateswaran are not of comparable intensities. The spectra of the molybdate and tungstate solutions show greater resemblance to telluric acid solution, the difference being that the Raman lines of longer shifts have greater values³ which however, depend on the magnitude of the force of binding.

4. The vibration ν_2 of the tetrahedron involves large changes in polarisability, larger than ν_4 , as the vibration spectra of all tetrahedral molecules show, but Venkateswaran's picture of (sodium) molybdate indicates the contrary. (Venkateswaran's $\nu_2 = 241$ (o) ; $\nu_4 = 317$ (4).

5. The values of the force constants for Mo-O and W-O bonds differ sharply from each other, Mo-O = 6.1×10^5 and W-O = 4.5×10^5 dynes per cm. This is not expected from their homologous positions in the periodic table. The force constant values may be expected to differ from those obtained for the sulphur-selenium sub-group of elements, but should agree among themselves. Values for inter-atomic distances obtained from X-ray analysis do not also indicate such a difference in the values of the binding forces.¹⁹ (Mo-O = W-O = 2.00 Å).

6. It is usually found that the breathing vibration of the tetrahedron possesses lower frequencies with increasing mass of the central atom, *e.g.*, in SO_4^{2-} , SeO_4^{2-} , (983:835 ; A.W. of central atom 32:79), or CCl_4 , SiCl_4 , TiCl_4 , SnCl_4 (459:425:382:367 ; A. W. 12:28:48:119). The contrary is met with in the case of molybdate and tungstate ions in solutions (895:925 ; A.W. of central atom 96:184), which may be explained if the binding force increases with the atomic weight ; but Venkateswaran's calculations show that with increase in the mass of the central atom, the value of the force constant falls sharply.

It is therefore believed that the extra lines 452 for WO_4^{2-} and 241 for MoO_4^{2-} recorded by Venkateswaran are either spurious or due to impurities like the isopoly complexes present in the solutions in which care was not taken to maintain a pH value greater than 8. It is unfortunate that Dr. Venkateswaran did not specify the pH values of his solutions,²⁰ although previous experimenters like Ghosh and Das²¹ or Damaschun²² did.

Accepting, however, the presence of only three lines in the vibration spectra of aqueous normal molybdate and tungstate solutions, the question arises as to why it should be three in number and not four, as the four vibrations of the tetrahedron (three of which are degenerate) are all allowed in Raman effect. There appears to be little doubt, as Venkateswaran also admits (in the case of the molybdate ion in solution),²⁰ that in solutions these ions have more complicated structure than a regular tetrahedron. It was suggested by the present author³

that the tetrahedral ions MoO_4^- and WO_4^- in aqueous solutions may have attracted two polar molecules of water to form dihydrated octahedral ions for reasons described in the introduction of this paper. An alternative possibility of the ion becoming a plane square²³ is rejected, since planar 4-covalent hexavalent molybdenum compounds are not known. There is *a priori* no reason to believe that the arrangement will remain identical in the solids where lattice forces and the process of dehydration come into play, and the fact that even in solids the two molecules of water persist in the molecule as water of crystallisation²⁴ was taken as some evidence for the existence of an attractive force between the central molybdenum and tungsten atom and the water molecules. A further support for the octahedral structure was obtained in the experimental fact that the approximate relation, $\nu_1^2 = \nu_2^2 + \frac{3}{2} \nu_3^2$ among the three fundamental frequencies of the octahedral molecule that are allowed in Raman effect¹³ holds almost accurately between the three Raman frequencies recorded for the molybdate and tungstate ions in solution. The objection raised¹¹ that ν_1^2 may never be equal to $\nu_2^2 + \frac{3}{2} \nu_3^2$, since the difference

$$\nu_1^2 - (\nu_2^2 + \frac{3}{2} \nu_3^2) = \frac{6(k' + k'' + i)}{4 l^2 \pi^2 c^2 m_n}$$

on the basis of Nagendranath's treatment,¹¹ appears to the present author to be without significance, since the value of the expression on the right side of the equation is not a constant quantity for all molecules, but is derived from the frequencies, and an approximate equality of ν_1^2 and $(\nu_2^2 + \frac{3}{2} \nu_3^2)$ does not seem to indicate any more than that in the ions of these transitional elements, the sum of the directed valence constant and the intravalence constant is a small quantity.

Alternative calculations have therefore been made here assuming octahedral structure for these ions in solution. Too great emphasis may not be laid on the exact magnitude of the forces obtained, since in coordination complexes like the stannichexachloride, which have some points of similarity with the coordinatively hydrated ions postulated here, Redlich²⁵ obtained apparently anomalous magnitude of the valence force. The values however, can well serve as comparative between themselves. Bright Wilson's equations¹³ have been used, because the values, although a little approximate, do not differ very much from those obtained from Nagendranath's more elaborate equations¹⁴ (*cf.* telluric acid).

TABLE III.

	ν_1	ν_2	ν_3	$k_{01} \times 10^{-5}$ dynes/cm.
Molybdate ion in solution	891	823	319	6.7
Tungstate ion in solution	929	834	320	7.1

The values are quite close to each other with that for the heavier ion slightly greater, as might be expected. It is also perhaps important to note that the value for Mo-O obtained here on assuming the octahedron does not greatly differ from that obtained from the frequencies of ammonium paramolybdate crystal (and solution) by Venkateswaran. It seems to indicate that no precipitous change in the magnitude of the valence force of the central atom is attendant with the process of hydration and rearrangement of configuration of the ion in solution. The process may be exactly similar in the case of the tungstate ion too, although experimental results from which similar calculations can be made are not available.

Systematic studies of the isopoly complexes like the para-molybdates and para-tungstates, and of the heteropoly complexes like silico-tungstic acid, etc., have been undertaken. Results have been obtained which are being expected to help understanding the structure of some of these complex bodies which are now being so extensively investigated, and will be published in a subsequent paper.

The author is indebted to Sir P. C. Ray and Prof. D. M. Bose for their kind interests, and to Dr. S. C. Sirkar for his guidance.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA,

REFERENCES.

- ¹ Ramaswamy, *Ind. J. Phys.*, **5**, 193 (1930).
- ² Ganesan, *Proc. Ind. Acad. Sci.*, **1**, 156 (1934).
- ³ Gupta, *Nature*, **140**, 685 (1937); Venkateswaran, *Chem. Sci.*, **6**, 5 (1937), *Proc. Ind. Acad. Sci.*, **7**, 144 (1938).
- ⁴ Gupta, *loc. cit.*
- ⁵ Funk, *Ber.*, **33**, 3700 (1900).
- ⁶ Molybdenum—Mauro, *Gazz. Chim. Ital.*, **18**, 120 (1888); Werner, *Z. anal. Chem.*, **9**, 407 (1895); Weinland and Knoll, *Ibid.*, **44**, 81 (1905); Rosenheim and Koss, *Ibid.*, **49**, 151 (1906); Spittle and Wardlaw, *J. C. S.*, 1748 (1931); Morgan, *Inorganic Chemistry*, 180 p. (Heller, 1936); Tungsten—Marchetti, *Z. anal. Chem.*, **10**, 760 (1879); Olsson, *Ber.*, **46**, 581 (1913); etc.
- ⁷ Chilesotti, *Gazz. Chim. Ital.*, **34** (2), 493 (1904); Morgan, *Inorganic Chemistry*, pp. 179, 180, 182 (1936). Also cf. Briggs, *Phil. Mag.*, **2** (vii), 1026 (1926).
- ⁸ Morgan, *Inorganic Chemistry*, 26 p. (1936).
- ⁹ Hultgren, *Phys. Rev.*, **40**, 891 (1932).

- ¹⁰ Sidgwick, *Cornell University Lectures*, p. 213 (1933) ; Morgan, *Inorganic Chemistry*, 80 p. (1936) ; etc
- ¹¹ Venkateswaran, *Proc Ind Acad Sci.*, **7**, 144 (1938).
- ¹² Meyer and Franke, *Z. anorg. Chem.*, **193**, 191 (1930).
- ¹³ Yost, Steffens and Gross, *J. Chem. Phys.*, **2**, 313 (1934).
- ¹⁴ Nagendranath, *Proc Ind. Acad. Sci.*, **1**, 250 (1934).
- ¹⁵ Rosenheim, *Abegg's Handbuch der anorg. Chem* , Bd. IV, Abt. 1, 2te Heft, p. 608 ; *Z. anorg. Chem.*, **96**, 139 (1916)
- ¹⁶ Jander, *Z. anorg Chem.*, **194**, 383 (1931).
- ¹⁷ Middleton, *J. Chem. Ed.*, **10**, 726 (1933).
- ¹⁸ Friend, *Inorganic Chemistry*, Vol. VII, Part III, p. 193 (Griffin, 1926).
- ¹⁹ Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, **VIII**, (Oslo, 1927).
- ²⁰ Venkateswaran, private communication to the author.
- ²¹ Ghosh and Das, *J. Phys. Chem.*, **36**, 586 (1932).
- ²² Damaschun, *Z. phys. Chem.*, **16**, 81 (1932).
- ²³ Bright Wilson, *J. Chem. Phys.*, **2**, 432 (1934).
- ²⁴ Funk, *loc. cit.*
- ²⁵ Redlich, Kurz and Rosenfeld, *Z. phys Chem.*, **19B**, 231 (1932)

THE THEORY OF ABSORPTION IN IONISED GAS

I. Opacity in Stellar Material. II. Optical Properties of Liquid Metals.

BY BIBHA MAJUMDAR, M A.
(PREMCHAND ROYCHAND SCHOLAR)
Bose Research Institute, Calcutta

(Received for publication, June 14, 1938.)

ABSTRACT. In §1 a quantum theory of absorption of electromagnetic radiation by ionised gas is worked out, in which the electrons take up energy from the electric field of the incident radiation and transform it by collisions with ions to random motion of electrons and ions. In §2 the theory is applied to calculate the opacity coefficients in stellar interior and the results are compared with those obtained by Eddington from Kramers' process of absorption for a free-free transition. In §3 the optical properties of liquid metals are studied from this general theory and found to agree fairly well with the observations.

INTRODUCTION.

The opacity of the stellar matter is mainly due to the fact that the gases composing the stars are ionised to a high degree. So also the absorption of electromagnetic waves in liquid metals can be explained, as will be discussed later, under the assumption that it consists of free electrons moving in the field of the ions. The view that an ionised gas may be very opaque to the exposed radiation has been demonstrated in the laboratory by Anderson¹ and others. In this experiment a fine metallic wire was suddenly made to explode by passing a heavy discharge through it from a large condenser as a result of which the gas, thus formed, emitted a continuous spectrum crossed by dark lines produced by its cooler outer portions, the presence of enhanced lines showing that even the cooler parts were ionised. Subjecting the gas to a radiation from another spark behind it Anderson found that its opacity was very high.

What is then the mechanism that an ionised gas may put hindrance to the incident radiation and become opaque? A free electron, when encountering an ion or even a neutral atom may switch off from a state of lower energy to that of a higher one by absorbing a requisite quantum of energy from the incident radiation, the reverse process being that an electron in encountering is accelerated in the potential field of the ion and accordingly emits a corresponding quantum of energy as required by the classical electrodynamics. The electron in the atom,

if it is not completely ionised, may also absorb energy by photo-electric process and leaves the ion with a kinetic energy depending on the amount of radiation received. The reverse process is the capture of the electron by the ion with requisite amount of emission of radiation. The first process is usually known as the absorption or emission by free-free transition and the latter is by bound-free transition. The absorption and emission spectra as observed in X-rays are attributed to these causes. Another mechanism may, however, be possible where free electrons take up energy from the electric field of the incident radiation and transform it by collisions with ions to random motions of electrons and ions, that is, to heat in a gas. This process has been considered to be the cause of absorption of radiation in metals in Drude's representation.

The first successful theory of absorption for free-free and bound-free transitions of the electron is due to brilliant researches of Kramers.² Following classical electrodynamics Kramers calculated the amount of radiation emitted within a certain frequency range by an electron during its encounter with an ion and since in thermodynamic equilibrium the coefficients of emission and absorption are connected by the well-known Einstein's relation, the corresponding absorption was then easily found out. Applying Bohr's correspondence principle in a very ingenious manner he succeeded in calculating the distribution of intensity in a continuous spectrum, which agreed strikingly well with the observations of Kulenkampff on X-rays. Inspired by the success of Kramers' theory Eddington³ extended his method of calculation to investigate the opacity coefficients in the interior of stars, which, as mentioned, consists of a system of highly ionised gas, subject to a radiation field having the same quality as soft X-rays emerging from the deep interior. He evaluated the opacity coefficients for the absorption of radiation particularly by the processes of switching off of electron from one orbit to the other at encounters with the ions, *i.e.*, for free-free transitions, and applied it extensively in his theory of the internal constitution of the stars. The opacity due to free-free transitions is no doubt predominant in the deep interior of the stars where the atoms are almost completely ionised and hence much simpler. The extension of similar calculations for the atmospheres of the stars is however no simple matter. Firstly, because of the comparatively low temperature the atoms retain most of their electrons and thus favouring the contributions of the bound-free photo-electric ionisation process to the opacity and secondly the atoms are found to be existing in different stages of ionisation and excitations.* A pioneer attempt in this direction was however made by Milne⁴

* The opacity of stellar atmospheres, specially for later type stars may also come, as pointed out by Pannekoek, from the interaction of free electrons with neutral hydrogen atoms. The electrons are supposed to come from the more easily ionised metals and tend to interact with the neutral hydrogen atoms rather than with their own positive ions because of the relatively high abundance of the former. Investigation in this direction is being carried out in the light of the theory we have developed in the present paper and will be published shortly.

who managed to calculate the opacity coefficients due to photoelectric ionisation of the atoms taking into account their different stages of ionisation under the circumstances existing in the stellar atmospheres and utilised the results successfully for interesting investigations about the structure and other physical properties of the stellar atmospheres. Notwithstanding the great success of Eddington's theory, his quantitative estimation of the value of the opacity coefficient failed, however, to agree with the results obtained from astronomical observations. As for example the calculated coefficient of opacity in the case of Capella was less than that as obtained from the Mass-Luminosity curve by a factor of the order of ten. This discrepancy gave rise to many interesting speculations by Eddington and Strömberg⁵ as regards the abundance of different elements, particularly that of hydrogen existing in the stars. This discrepancy together with the recent theory of stellar structure proposed by Milne⁶ that a star is composed of an abnormally high density core at the centre surrounded by a diffuse layer of gas, led a number of workers⁷ to investigate the problem afresh from the modern developments of Physics. Applying the more recent theory of continuous absorption as worked out by Oppenheimer, Gaunt, Sommerfeld, Stobbe⁸ and others from new quantum mechanics, they calculated the opacity coefficients both in diffuse and condensed gas obeying Maxwellian as well as Fermi Statistics respectively. In the former case they obtained results which are essentially the same as Eddington's, whereas for the latter case the result is not only different in magnitude from that of Eddington but also predicts a different law for the opacity coefficient with regard to density and temperature.

In the present paper we have thought of a plan of investigation of the theory of absorption coefficient from a standpoint different from Kramers-Eddington-Milne. We have adopted the third alternative process of absorption as mentioned above. In this procedure we calculate the absorption coefficient from the study of conduction in the ionised gas with the help of the phenomenological theory of Maxwell. It further allows us to calculate the refractive index of the system. Such a theory of absorption was originally developed by Drude, Lorentz and others in connection with the free electron theory of the optical properties of metals. A rigorous theory has been recently worked out by Kronig,⁹ and others with the help of quantum mechanical conceptions and yielded results in agreement with the observations. The idea of calculation of opacity from Drude-Lorentz theory was contained in a very suggestive paper of Stewart¹⁰ in 1922 and has been revived again by Kothari¹¹ and Hund¹² in recent years. It will be interesting to calculate absorption as well as opacity coefficients from the analogous quantum mechanical procedure of Kronig and then to compare the results with those derived from the Kramers-Eddington mechanism. The optical properties of liquid metals are also calculated and shown side by side for a better understanding of the mechanism of absorption under question.

In the first article a general mathematical theory of absorption is worked out in a system of ionised gas, subject to an external field of radiation. In the second article the theory is applied to find out the opacity coefficients in the interior of stars and the results are discussed in reference to the absorption theory developed by Kramers, Eddington and others. In the last article the optical properties of liquid metals are worked out.

MATHEMATICAL FORMULATION OF THE PROBLEM.

§1. Let us now come straight to our problem. We have got a system of gas mixture consisting of ions and electrons which are detached from the parent atoms either by temperature or by pressure and subject to an external electromagnetic field of radiation. The resultant change in the distribution function f of the electrons, due to electric field of radiation as well as to the interaction between the ions and electrons, assuming no energy being interchanged between them during the process, is given by the usual Boltzmann's equation

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_{\text{field}} + \left(\frac{\partial f}{\partial t} \right)_{\text{collision}} \quad \dots (1)$$

Or, writing explicitly we obtain

$$\frac{\partial f}{\partial t} + \frac{h}{m} \mathbf{k} \cdot \frac{\partial f}{\partial \mathbf{x}} + \frac{e\mathbf{E}}{h} \cdot \frac{\partial f}{\partial \mathbf{k}} + \iiint W(\mathbf{k}\mathbf{k}') [f(\mathbf{k}) - f(\mathbf{k}')] d\mathbf{k}' dk_y' dk_z' = 0, \quad \dots (2)$$

where the group-velocity of the electron is given by $\vec{v} = \frac{h}{m} \vec{k}$, $\vec{k}$ being the wave vector.

The total Lorentz force $\vec{F}$ acting on the electron is given by

$$\vec{F} = e\vec{E} + \frac{e}{c} [\vec{v} \times \mathbf{H}] ; \quad \dots (3)$$

but we have neglected the force due to the magnetic field $\mathbf{H}$ of the incident wave,

which is of the order of $\frac{1}{c} \frac{v}{c}$ compared with that of the electric field and hence very small.

$\vec{W}(\vec{k} \vec{k}')$ denotes the probability of transition of the electron from a state $\vec{k}$ to the state $\vec{k}'$ and the intensity of the electric field is

$$E = E_0 e^{i\omega t}, \quad \dots (4)$$

where $\nu = \frac{\omega}{2\pi}$ is the frequency of the wave.

To solve equation (2) we put

$$f = f_0 + f_1, \quad f_1 \ll f_0 \quad \dots (5)$$

f_0 , the Fermi distribution function without the field, is given in usual notation, by

$$f_0 = \frac{1}{A e^{\epsilon/kT} + 1} \quad \dots (6)$$

For f_1 , the distribution due to perturbation, we assume

$$f_1 = e^{i\omega t} k_x \chi(\vec{k}), \quad \dots (7)$$

where $\chi(\vec{k})$ depends only on the magnitude of $\vec{k}$ but not on its direction. Further let us introduce the time of relaxation τ as defined by

$$\left(\frac{\partial f}{\partial t} \right)_{\text{collision}} = -\frac{f_1}{\tau} \quad \dots (8)$$

whence we obtain on substitution of (5) in equation (2) and with the help of (4) (6), (7) and (8),

$$i\omega\chi - \frac{h}{m} e^{-i\omega t} \frac{\partial f_0}{\partial \epsilon} \left(\frac{kT}{A} \frac{\partial A}{\partial x} + \frac{\epsilon}{T} \frac{\partial T}{\partial x} \right) + \frac{eh}{m} E_0 \frac{\partial f_0}{\partial \epsilon} + \frac{\chi}{\tau} = 0 \quad \dots (9)$$

If we assume that the system is homogeneous and there is no temperature gradient we must put $\frac{\partial A}{\partial x}$ and $\frac{\partial T}{\partial x}$ equal to zero, so that the equation (9) is reduced to

$$(1 + i\omega\tau)\chi + \tau \frac{eh}{m} E_0 \frac{\partial f_0}{\partial \epsilon} = 0 \quad \dots (10)$$

giving

$$\chi = - \frac{\tau \frac{eh}{m} E_0 \frac{\partial f_0}{\partial \epsilon}}{1 + i\omega\tau} \quad \dots (11)$$

Having thus obtained χ , we can at once find f_1 from (7) and hence the current. We thus obtain the current

$$I_x = 2e \iiint v_x f dk_x dk_y dk_z$$

$$= - \frac{16\pi e^2 (2m)^{\frac{1}{2}}}{3h^3} P \int \frac{e^{\frac{3}{2}} \frac{\partial f_0}{\partial \epsilon} (\Delta - i\omega) d\epsilon}{\Delta^2 + \omega^2} \quad \dots (12)$$

where $\Delta = \frac{v}{\tau}$ = the number of collisions per second.

Now to calculate the absorption of the incident radiation we compare our expression for current with that as given by the phenomenological theory of Maxwell, which runs as follows

$$I_x = \sigma I_0 + \frac{\epsilon_d - 1}{4\pi} i\omega I_0 \quad \dots (13)$$

where σ , the conductivity, and ϵ_d the dielectric constant of the medium, are connected with the extinction coefficient κ and the refractive index μ as follows :

$$\left. \begin{aligned} \mu^2 - \kappa^2 &= \epsilon_d \\ \mu\kappa &= \frac{\sigma}{\omega} \end{aligned} \right\} \quad \dots (14)$$

The extinction coefficient κ is here defined as such that the intensity of the wave after travelling through a distance $\frac{c}{2\pi\omega\kappa}$ will be diminished to $\frac{1}{e}$ th of its original intensity.

From (12) and (13) we obtain,

$$\sigma = P \int \frac{e^{\frac{3}{2}} \frac{\partial f_0}{\partial \epsilon} \Delta d\epsilon}{\Delta^2 + \omega^2} \quad \dots (15)$$

$$\frac{\epsilon_d - 1}{4\pi} = -P \int \frac{e^{\frac{3}{2}} \frac{\partial f_0}{\partial \epsilon} d\epsilon}{\Delta^2 + \omega^2} \quad \dots (16)$$

$$P = \frac{16\pi e^2 (2m)^{\frac{1}{2}}}{3h^3} \quad \dots (17)$$

which when substituted in (14) give us the extinction coefficient as well as the refractive index as follows :

$$\mu^2 - \kappa^2 = 1 - 4\pi P \int \frac{-e^{\frac{3}{2}} \frac{\partial f_0}{\partial \epsilon} d\epsilon}{\Delta^2 + \omega^2} \quad \dots \quad (18)$$

$$\text{and} \quad \mu\kappa = \frac{1}{v} \int \frac{-e^{\frac{3}{2}} \frac{\partial f_0}{\partial \epsilon} \Delta d\epsilon}{\Delta^2 + \omega^2} \quad \dots \quad (19)$$

1. The Opacity Coefficients in Stellar Interior.

§ 2. The opacity coefficient, *i.e.*, the mean value of the absorption coefficient taken over all frequencies after the method of Rosseland is defined by

$$\kappa = \frac{\int \frac{\partial I_\nu}{\partial T} d\nu}{\int K_\nu \frac{\partial I_\nu}{\partial T} d\nu} \quad \dots \quad (20)$$

where I_ν is the intensity of black body radiation and is given by Planck's formula

$$I_\nu = \frac{B\nu^3}{e^{h\nu/kT} - 1}, \quad B = \frac{8\pi h}{c^2} \quad \dots \quad (21)$$

$$\frac{\partial I_\nu}{\partial T} = \frac{Bh}{kT^2} \cdot \frac{\nu^4 e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2} \quad \dots \quad (22)$$

and K_ν , the mass absorption coefficient, *i.e.*, the absorption coefficient per gram per sq. cm. is connected with our extinction coefficient by the relation

$$K_\nu = \frac{4\pi\kappa\nu}{c\rho} \left(1 - e^{-h\nu/kT}\right), \quad \dots \quad (23)$$

the factor $\left(1 - e^{-h\nu/kT}\right)$ giving the influence of the stimulated radiation.

With the help of these formulae we now proceed to evaluate the astronomical opacity coefficients.

At the beginning we must have an expression for Δ , the collision frequency which is involved in the integrals (18) and (19). We assume a general potential field between the electron and the ion of the form

$$V(r) = -\frac{Ze^2}{r} e^{-r/b}, \quad \dots (24)$$

where Z is the number of free electrons per atom and b the so called screening constant which gives the effect of the interaction of the other electrons and ions and is only a small fraction of the average distance between the ions. With this value of the potential field, the expression for Δ can be obtained as^{1,2*}

$$\Delta = \frac{\pi Z^2 e^4 n^2 J}{(2m)^2 e^2}, \quad \dots (25)$$

where $J = \log(l+1) - \frac{l}{l+1}, \quad \dots (26)$

$$l = \frac{32\pi^2 m e b^2}{h^2} \quad \dots (27)$$

$$= 6.63 \cdot 10^{27} e b^2 \quad \dots (28)$$

For ordinary stars (Giants and Dwarfs) where the electrons are distributed according to the Maxwellian Law, we obtain from (18) and (19), after integration, provided $\frac{\Delta}{\omega} \ll 1$.

$$\mu^2 - \kappa^2 = 1 - \frac{n e^2}{\pi m v^2} \quad \dots (29)$$

$$= 1 - \frac{e^2 \rho}{\pi m \mu_m m_n v^2} \quad \dots (30)$$

* It may be interesting to calculate the opacity coefficient for the radiative resistance, i.e., for the reaction on the electron due to its own radiation. We obtain in this case also an analogous Δ , the collision term, given by

$$\Delta = \frac{8\pi^2 e^2 v^3}{3m c^3}$$

Following a similar method as indicated in the text it can be easily verified that the absorption coefficient is independent of the frequency of the incident radiation and we obtain for the opacity coefficient

$$K = \frac{8\pi e^4}{3 m^2 c^4 \mu m_n}$$

It is just what we would obtain from Thomson's scattering for free electrons,

$$\text{and} \quad \mu_K = \frac{2e^6 z^2 n^+ n^-}{3 (2\pi m k T)^{\frac{3}{2}} v^3} G \quad \dots (31)$$

$$= \frac{2e^6 z^2 \rho^2}{3 (2\pi m k T)^{\frac{3}{2}} \mu_m A m_u^{\frac{3}{2}} v^3} G \quad \dots (32)$$

where ρ = density

μ_m = the mean molecular weight of the stellar material

A = the atomic weight

m_u = mass of the hydrogen atom.

$$G = -e^{kT_a} \cdot \frac{1}{kT_a} \text{Ei} \left(-\frac{1}{kT_a} \right) \quad \dots (33)$$

The function $\text{Ei}(-\beta)$ being defined by

$$-\text{Ei}(-\beta) = \int_{\beta}^{\infty} \frac{e^{-u}}{u} du \quad \dots (34)$$

$$\beta = \frac{1}{kT_a} \quad \dots (35)$$

The function is tabulated in Jahnke-Emde's *Functionen Tafeln*, pp. 78-86, 1933, and has got the following limiting values :—

$$-\text{Ei}(-\beta) = -\gamma + \log \frac{1}{\beta} + \beta - \frac{1}{4} \beta^2, \text{ for } \beta \text{ small} \quad \dots (36)$$

$$\text{and} \quad -\text{Ei}(-\beta) = e^{-\beta} \left(\frac{1}{\beta} - \frac{1}{\beta^2} + 2 \cdot \frac{1}{\beta^3} - \dots \right) \text{ for } \beta \text{ large} \quad \dots (37)$$

$$\text{where} \quad \gamma = \text{Euler's constant} = 0.577 \quad \dots (38)$$

In the case we are considering, $\beta \left(= \frac{1}{kT_a} \right)$ is small as can be easily verified and we therefore obtain

$$G = \log(kT_a) - \gamma - 1 \quad \dots (39)$$

For the white Dwarf stars where the electrons are in a degenerate state obeying the Fermi Distribution Law, we are concerned only with the value of Δ for

$$\epsilon = \epsilon_{\max} = \frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{\frac{2}{3}}$$

Putting Δ_0 for that value of Δ , we obtain from (18)

and (19), for $\frac{\Delta_0}{\omega} \ll 1$

$$\mu^2 - \kappa^2 = 1 - \frac{nc^2}{\pi m v^2} = 1 - \frac{c^2 \rho}{\pi m \mu_m m_n v^2} \quad \dots (40)$$

$$\text{and} \quad \mu \kappa = \frac{4z^2 c^6 n^+ J_0}{3 h^3 v^3}, \quad \dots (41)$$

$$= \frac{4z^2 c^6 \rho J_0}{3 h^3 \Lambda m_n v^3}, \quad \dots (42)$$

where J_0 is the value of J for $\epsilon = \epsilon_{\max}$.

Now as the evaluation of κ from the equations (30) and (32) or from (40) and (42) and the consequent evaluation of the Rosseland mean of the resulting K_ν are very complicated we shall be content with working out of the opacity coefficient under the assumption $\mu \sim 1$.*

* We can obtain at least a qualitative estimation of the value of μ as well as of the magnitude of Δ if we remember that in taking the Rosseland mean of a quantity depending on frequency almost all the contributions come from a region very near about a value of $\nu \sim \frac{5kT}{h}$

We thus obtain from (25) for ordinary stars where $\epsilon = \frac{3}{2}kT$,

$$\left(\frac{\Delta}{\omega}\right) = \frac{c^4 h}{5 \cdot 3^{\frac{1}{2}} m^{\frac{1}{2}} k^{\frac{5}{2}} m_n} \cdot \frac{z^2 J_0}{\Lambda T^{\frac{5}{2}}} = 1 \cdot 2 \cdot 10^{12} \cdot \frac{z^2 J_0}{\Lambda T^{\frac{5}{2}}} \quad \dots (43)$$

Also, for white Dwarf stars, we have

$$\left(\frac{\Delta_0}{\omega}\right) = \frac{8\pi c^4 m z J_0}{15 h^2 k T} = 1 \cdot 3 \cdot 10^4 \cdot \frac{z J_0}{T} \quad \dots (44)$$

Again from (30) and (40), we obtain for ordinary as well as white Dwarf stars,

$$\mu^2 - \kappa^2 = 1 - \frac{c^2 h^2 \rho}{25 \pi m \mu_m m_n k^2 T^2} = 1 - 4 \cdot 4 \cdot 10^9 \cdot \frac{\rho}{\mu_m T} \quad \dots (45)$$

Further from (32), for ordinary stars,

$$\mu \kappa = \frac{2 c^6 h^3}{125 (2 \pi m)^{\frac{3}{2}} m_n^{\frac{1}{2}} k^{\frac{3}{2}}} \cdot \frac{z^2 \rho J_0}{\Lambda \mu_m T^{\frac{3}{2}}} = 3 \cdot 6 \cdot 10^{21} \cdot \frac{z^2 \rho J_0}{\Lambda \mu_m T^{\frac{3}{2}}} \quad \dots (46)$$

and from (42), for white Dwarf stars,

$$\mu \kappa = \frac{4 c^6}{125 m_n k^3} \cdot \frac{z^2 \rho J_0}{\Lambda T^3} = 2 \cdot 9 \cdot 10^{13} \cdot \frac{z^2 \rho J_0}{\Lambda T^3} \quad \dots (47)$$

We therefore obtain from (32), (42) and (23),

for ordinary stars,

$$K_{\nu} = \frac{8\pi e^6 z^2 \rho G}{3c(2\pi mk'T)^3} \frac{e^{-h\nu/k'T} (e^{h\nu/k'T} - 1)}{\bar{A} m_u^2 \mu_m \nu^2} \quad \dots (18)$$

$$\text{and for white Dwarf stars } K_{\nu} = \frac{16\pi z^2 e^6}{3h^3 c \nu^2} \frac{J_0}{\Lambda m_u} e^{-h\nu/k'T} (e^{h\nu/k'T} - 1) \dots (49)$$

Or, taking Rosseland mean, for ordinary stars,

$$K = \frac{8\pi e^6 z^2 \rho G}{3c(2\pi mk'T)^3 \Lambda m_u^2 \mu_m} \frac{\int_0^{\infty} \frac{\partial I_{\nu}}{\partial T} d\nu}{\frac{Bh}{k'T^2} \int_0^{\infty} \frac{\nu^6 e^{2h\nu/k'T}}{(e^{h\nu/k'T} - 1)^3} d\nu} \quad \dots (50)$$

$$\text{Now since } \int_0^{\infty} \frac{\partial I_{\nu}}{\partial T} d\nu = \frac{B}{T} \left(\frac{k'T}{h} \right)^4 4! \beta_1$$

$$\text{and } \frac{Bh}{k'T^2} \int_0^{\infty} \frac{\nu^6 e^{2h\nu/k'T}}{(e^{h\nu/k'T} - 1)^3} d\nu = \frac{B}{T} \left(\frac{k'T}{h} \right)^6 6! \beta_2$$

The results obtained at the centre of the different stars are tabulated below :

	$\left(\frac{\bar{\Delta}}{\omega} \right)$	μ	κ	G
Sun	6.8 10^{-4}	1	2.4 10^{-8}	3.2
Capella	6.6 10^{-5}	1	1.0 10^{-10}	6.7
Model Giant Star	1.01 10^{-4}	1	2.3 10^{-10}	6.2
Model White Dwarf Star	9.9 10^{-2}	.07	3.6	$J_0 = 1.4$

In the above calculations, the Sun, Capella and white Dwarf stars are taken to be composed of completely ionised iron atoms so that $z=26$, $A=56$ and $\mu=2.1$; whereas in the case of model Giant stars we take $z=25$, $A=50$, $\mu=1.9$. We thus obtain $\mu=1$ for the ordinary stars and $\mu=.07$ for white Dwarf stars. The opacity coefficient obtained for white Dwarf stars under the assumption $\mu=1$ should therefore be divided by .07.

where

$$\beta_1 = \sum_{n=1}^{\infty} \frac{1}{n^4} = 1.082$$

$$\beta_2 = \frac{1}{2} \left\{ \sum_{n=1}^{\infty} \frac{1}{n^5} + \sum_{n=1}^{\infty} \frac{1}{n^6} \right\} = 1.027$$

we obtain finally,

$$K = \frac{4\pi}{45} \cdot \frac{\beta_1}{\beta_2} \cdot \frac{z^2 e^{10} h^2 \rho_G}{c(2\pi m)^3 A m_u \mu_m} \cdot \frac{1}{k^2 T^2}$$

$$= 1.4 \cdot 10^{23} \cdot \frac{z^2 \rho_G}{A \mu_m T^2} \quad \dots (51)$$

For the case of completely ionised iron atoms,

$$K = 8.0 \cdot 10^{23} \cdot \frac{\rho_G}{T^2} \quad \dots (52)$$

Similarly for stars of white Dwarf type we obtain

$$K = \frac{8\pi}{45} \cdot \frac{\beta_1}{\beta_2} \cdot \frac{z^2 c^6 J_0}{h c A m_u} \cdot \frac{1}{k^2 T^2}$$

$$= 1.1 \cdot 10^{15} \cdot \frac{z^2 J_0}{A T^2} \quad \dots (53)$$

Or, for white Dwarf stars composed of completely ionised iron atoms,

$$K = 1.3 \cdot 10^{16} \cdot \frac{J_0}{T^2} \quad \dots (54)$$

The opacity coefficients obtained for different stars are as follows* :—

* It may be pointed out that almost similar results could also be obtained directly from (23) by substituting $\nu \sim \frac{5kT}{h}$ and taking the value of κ as tabulated in the foregoing footnote.

We thus obtain

$$K = \frac{20\pi k}{ch} (1-e^{-5}) \frac{\kappa T}{\rho} = 43 \frac{\kappa T}{\rho} \quad \dots (55)$$

i.e., 54, 32, 60 and $1.5 \cdot 10^3$ for Sun, Capella, model Giant Star and model white Dwarf Star respectively.

Name	Opacity Coefficient (K) from our result	Opacity from Eddington's result.
Sun	·48	·074
Capella	·30	·022
Model Giant Star	·63	·05
Model White Dwarf Star*	$1·3 \cdot 10^3$	$3·12 \cdot 10^3$

Comparing these results with those obtained from Kramers-Eddington mechanism, we find that the present method yields a larger value of the opacity coefficient in stars consisting of non-degenerate electron gas while in the case of degenerate gas a smaller value is obtained.† (With $\mu \sim 0.7$, Eddington's value for the model white Dwarf star becomes much larger than that in the table.) It is to be particularly noticed that the value of the opacity coefficient in degenerate gas as obtained in the present paper does depend, though slightly on the density (logarithmic) in contrast to the value obtained by the previous workers, which was independent of density. The present method of treatment has the advantage of taking account of the effect of a screened coulomb potential field on the opacity, which plays evidently an important role in a system of ionised gas having a comparatively high density as we are concerned with in our present problem. It will be interesting to develop the present method of treatment to find out the relativistic opacity coefficient in degenerate as well as in non-degenerate electron gas system. This we hope to undertake in a subsequent work.

II. The Optical Properties of Liquid Metals.

§ 3. The explanation of the properties of metals considering them as made up of electrons and ions was, though initiated by Drude and Lorentz, only recently revived by Pauli, Sommerfeld, Bloch and others by incorporating quantum mechanical conceptions and postulating that the electrons obey the Fermi statistics. They assume thereby that the electrons are in a periodic potential inside the metal due to the lattice structure of the ions instead of being

* The value of the opacity coefficient obtained from (54) is here divided by .07 as mentioned in a previous footnote

† Though there is a slight uncertainty in evaluating b , the screening constant which is involved in our calculation, the order of its magnitude which we have assumed, is correct as can be easily verified from the application of Debye Hückel's theory or from the method used by Chapman (S. Chapman, M. N. R. A. S., 82, 392, 1922).

free in Drude's sense and calculate the conduction, etc., which are in reasonable agreement with the experiments. But the properties of the metal when it is heated till it melts are not yet definitely understood. In one model^{14*} it is assumed that the lattice structure is still retained even when the metal melts and although this explains fairly satisfactorily the phenomena of conductivity in some liquid metals in relation to solid states, it fails to account for the temperature dependence of conductivity in other liquid metals. In the second model¹⁵ it is assumed that because of relatively high temperature in a liquid metal the regular distribution of its ions in the form of lattice is not maintained so rigidly and the metal behaves in the extreme case almost like a gas mixture of electrons and ions distributed at random, the electrons still obeying the Fermi statistics. The interaction between the electrons and the ions is, in this case, considered practically elastic, the interaction potential being given by (24). The conductivity calculated in this model comes out practically independent of temperature† which is in fact the case for the majority of the liquid metals. These two models evidently represent the extreme cases of reality, the former one being perhaps valid near the melting point, and the latter much above this.

The X-ray investigation of the distribution of ions in liquid metals, however, definitely shows that the periodicity of the lattice ions does not exist at distances of the order of mean free path of the electron and electron can be assumed in a first approximation to move in the field of irregularly distributed ion groups. This model of fluid as first suggested by Debye and Menke¹⁶ has been thoroughly investigated by Schubert.¹⁷ He finds that the eigenfunction of the electron though different from a plane wave is distinctly non-periodical and the electron behaves, at least so far as the absorption of an electromagnetic wave is concerned, just like free electrons absorbing radiation of any frequency in a potential field of the type (24). We shall therefore apply our calculation of §1 where f_0 will be given by Fermi statistics to estimate the absorption as well as the refractive index in liquid metals.

We thus obtain from (18), (19) and (17) after integration,

$$\mu^2 - \kappa^2 = 1 - \frac{ne^2}{\pi m v^2} \cdot \left(1 + \frac{\Delta_0}{4\pi^2 v^2} \right) \quad \dots \quad (56)$$

* It is maintained that the atoms in a liquid metal vibrate about slowly varying mean positions with a frequency ν_0 and the change of resistance on melting can be accounted for by the change in atomic frequency of the solid metals.

† The slight temperature dependence of conductivity is, however, due to the thermal expansion of the liquid crystal.

and

$$\mu\kappa = \frac{4z^2 e^6 n^+ J_0}{3h^3 v^3} \cdot \left(1 + \frac{\Delta_0^2}{4\pi^2 v^2} \right) \quad \dots (57)$$

where n^+ is the number of ionised atoms in unit volume and Δ_0 and J_0 are the values of Δ and J respectively for $e = e_{\text{max}} = \frac{h^2}{8m} \left(\frac{3n}{\pi} \right)^{\frac{2}{3}}$ of the Fermi distribution.

$$\text{We get} \quad \Delta_0 = \frac{16\pi^2 e^4 m J_0 z}{3h^3} = 8.8 \cdot 10^{15} J_0 z \quad \dots (58)$$

$$\text{and} \quad J_0 = \log(t_0 + 1) - \frac{t_0}{t_0 + 1}; \quad t_0 = 38.2 z^{\frac{2}{3}} \left(\frac{b}{a} \right)^2. \quad \dots (59)$$

$\bar{a}$ being the average distance between the ions.

We can further express the above equations in the form

$$\mu^2 - \kappa^2 = 1 - \frac{5.4 \cdot 10^{10} \lambda^2 z \rho}{(1 + 2.2 \cdot 10^9 z^{\frac{2}{3}} J_0^2 \lambda^2) A} \quad \dots (60)$$

$$\mu\kappa = \frac{1.3 \cdot 10^{15} z^2 \rho \lambda^3 J_0}{(1 + 2.2 \cdot 10^9 z^{\frac{2}{3}} J_0^2 \lambda^2) A} \quad \dots (61)$$

where ρ is the density and A the atomic weight.

Let us now compare the results, calculated from (60) and (61) with the values obtained by Kent's¹⁸ experimentally. The comparison is shown in the following table:—

Metal.	Wave-length λ in $\mu\mu$.	$-(\mu^2 - \kappa^2)$ Expt.	$-(\mu^2 - \kappa^2)$ calculated.	$2\mu\kappa$ Expt.	$2\mu\kappa$ calculated.
Mercury	579	16.7	10.1	14.2	12.4
	546	15.2	9.9	12.3	11.4
	404	9.2	6.4	5.8	5.8
Lead	579	14.8	7.2	22.6	9.1
	546	14.5	7.0	20.7	8.4
	404	11.2	4.5	12.1	4.3
Cadmium	579	25.7	10.7	8.1	13.1
	546	23.1	10.5	7.4	12.1
	404	12.5	6.9	2.7	6.1
Tin	579	26.7	8.7	19.3	10.9
	546	25.5	8.5	18.4	10.0
	404	11	5.5	10	5.1
Bismuth	579	9.7	6.1	19.7	11.8
	546	9.2	6.0	18.0	11.0
	404	7.0	4.5	11.8	6.4

Taking into consideration of the uncertainty introduced by the screening constant b , which we have taken for the present case $b = \frac{\bar{a}}{6}$, the agreement between the theoretical and the experimental values may be said to be fairly satisfactory. Further, we have *ad hoc* assumed the number of free electrons per atom to be equal to the number of valency electrons, which also does not seem to be quite correct. The agreement of these values with the experiments, however, adds a genuine support to the astrophysical theories which we have applied particularly to the state of matter in white Dwarf stars. It further suggests the interesting fact that the state of matter in white Dwarf stars is like that in molten metals much above the melting point.

It is a great pleasure for me to acknowledge my heartiest thanks to Drs. R. C. Majumdar and D. S. Kothari for their continued discussions and valuable suggestions and to Profs. M. N. Saha and S. N. Bose for their kind interest and encouragement. I am also grateful to the authorities of the Bose Research Institute for kindly permitting me to carry on the present investigation in the Institute and to the Director, Dr. D. M. Bose for the interest he has taken in my work.

REFERENCES.

- ¹ J. A. Anderson, *Astro. Jour.*, **51**, 37 (1920); *Proc. Nat. Acad. Sci.*, **8**, 231 (1922).
- ² H. A. Kramers, *Phil. Mag.*, **46**, 836 (1923).
- ³ A. S. Eddington, *Internal Constitution of Stars* (1926); *M. N. R. A. S.*, **184**, 104 (1924).
- ⁴ E. A. Milne, *M. N. R. A. S.*, **85**, 750 and 979 (1925); *Ibid.*, **89**, 17 (1928).
- ⁵ A. S. Eddington, *M. N. R. A. S.*, **92**, 364 and 471 (1932); B. Strömberg, *Zs. f. Astrophysik*, **4**, 118 (1932); **7**, 222 (1933).
- ⁶ E. A. Milne, *M. N. R. A. S.*, **91**, 4 (1930); **92**, 610 (1932).
- ⁷ R. C. Majumdar, *Astro. Nach.*, **243**, 6 (1931); **247**, 217 (1932); D. S. Kothari and R. C. Majumdar, *Astro. Nach.*, **244**, 61 (1931); S. Chandrasekhar, *Proc. Roy. Soc. A*, **133**, 241 (1931); **135**, 472 (1932); B. Swirles, *M. N. R. A. S.*, **91**, 861 (1931); S. Rosseland, *Handbuch der Astrophysik*, **3**, 152 (1930).
- ⁸ J. R. Oppenheimer, *Zsf. phys.*, **55**, 725 (1929); J. A. Gaunt, *Phil. Trans. (A)*, **220**, 163 (1930); A. Sommerfeld, *Ann. d. phys.*, **41**, 257 (1931); M. Stobbe, *Ann. d. phys.*, **7**, 661 (1930).
- ⁹ R. de L. Kronig, *Proc. Roy. Soc. A.*, **124**, 409 (1929); **133**, 255 (1931); A. H. Wilson, *Proc. Roy. Soc. A.*, **181**, 274 (1935).
- ¹⁰ J. Q. Stewart, *Phys. Rev.*, **22**, 324 (1923).
- ¹¹ D. S. Kothari, *M. N. R. A. S.*, **93**, 61 (1932).
- ¹² F. Hund, *Ergeb. Exakt Naturwissenschaften*, **15**, 189 (1936).
- ¹³ R. C. Majumdar, *Zs. f. Phys.*, **9**, 706 (1934).
- ¹⁴ N. F. Mott, *Proc. Roy. Soc. A*, **126**.
- ¹⁵ R. C. Majumdar, *Proc. Nat. Inst. of Sc. of India*, **1**, 77 (1935).
- ¹⁶ P. Debye and Menke, *Phys. Zs.*, **31**, 797 (1930).
- ¹⁷ S. Schubert, *Phys. Zeit Sowjetunion*, **5**, 81 (1934).
- ¹⁸ C. V. Kent, *Phys. Rev.*, **24**, 459 (1919).

STRUCTURE OF AROMATIC COMPOUNDS, PART IV,* SPACE-GROUP AND ATOMIC ARRANGEMENTS IN PHLOROGLUCINE DIHYDRATE

By K. BANFRJEE, D.Sc.
Reader in Physics, Dacca University

AND

RAJIUDDIN AHMAD, M.Sc.

(Received for publication, June 22, 1938.)

ABSTRACT. An analysis of phloroglucine dihydrate by X-rays is described. The axial lengths are $a_0=6.80$, $b_0=8.103$ and $c_0=13.70$ in Angstrom units. The $o k l$ planes are absent when $k+l$ is odd and $h o l$ planes are absent when $h+l$ is odd. So the space-group is D_{2h}^{12} P n n m. The density of the crystal is found to be 1.391 gms. per c.c., hence there are 4 molecules per unit cell. Molecular orientation in the crystal lattice is determined from considerations of magnetic anisotropy and space-group.

Phloroglucine dihydrate is a compound in which three hydrogen atoms of a benzene ring are replaced by monovalent OH groups in symmetrical positions, and there are two molecules of water of crystallisation per molecule of phloroglucine. It has the chemical formula $C_6H_3(OH)_3 \cdot 2(H_2O)$. From the crystallographic descriptions of this substance given in Groth's *Chemische Kristallographie*, Vol. IV, p. 89..., it belongs to the orthorhombic bipyramidal class with axial ratios.

$$a:b:c=0.8261:1:3.4172.$$

Crystals were obtained from a solution in alcohol, and $m(110)$ and the $c(001)$ faces were found to be well-developed.

The cell dimensions were determined by rotation photographs about the three crystallographic axes in a cylindrical camera of diameter 8.416 cm. which was calibrated by powder photograph of an aluminium wire. Copper K_α radiation from a Hadding tube was used for the purpose. The following values were found for the axial lengths :—

$$a_0=6.79\text{\AA}, \quad b_0=8.10\text{\AA} \quad \text{and} \quad c_0=13.70\text{\AA}.$$

The density of the substance was determined by Retger's suspension method from a solution of zinc sulphate in water and was found to be 1.391 gm. per c.c. and hence the number of molecules per unit cell comes out to be 4.

* Communicated by the Indian Physical Society.

Oscillation photograph about a and b axes were taken, the range of oscillation being 10° . The reflecting planes were identified with the help of Bernal's chart.¹ The results are given in the tables I—III. From an examination of the list of reflecting planes tabulated there it will be seen that $o k l$ planes are absent when $k + l$ is odd and $h o l$ planes are absent when $h + l$ is odd. There are no other systematic absent planes. Hence the space-group is $D_{2n}^{12} Pnmm$. The total number of symmetry elements possessed by the crystal is 8 and there are 4 molecules per unit cell. Hence corresponding to the above space-group each molecule must possess a plane of symmetry parallel to either (001) or (010) plane.

TABLE I.

Axial Planes.

Indices.	Estimated Intensity.	Indices.	Estimated Intensity
004	W	00(16)	VW
006	VS	020	VW
008	MS	040	VW
00(10)	S	200	MS
00(12)	S	400	VS
00(14)	MW	600	MS

TABLE II.

Prism Planes.

Indices.	Estimated Intensity.	Indices	Estimated Intensity.
013	VS	01(17)	MW
015	S	022	S
017	VVW	024	MS
019	S	026	W
01(11)	MW	028	M
01(13)	VW	02(10)	VW

TABLE II (contd.).

Prism Planes.

Indices.	Estimated Intensity.	Indices.	Estimated Intensity.
02(12)	W	082	MS
02(14)	W	086	W
031	S	08(10)	W
033	VS	091	W
035	S	093	W
039	MS	095	VW
03(11)	W	097	VW
03(13)	VW	0(10)2	W
042	M	0(10)4	VW
044	W	101	M
046	W	103	VW
048	MS	105	VW
04(10)	VW	109	MS
04(12)	MS	10(11)	MS
051	M	202	VS
053	W	204	VS
055	MS	206	W
057	MS	208	W
059	VW	20(10)	M
05(11)	M	20(12)	MW
05(15)	VVW	20(16)	VW
066	MS	307	VVW
06(10)	MS	30(11)	S
06(12)	VVW	402	W
071	W	404	MW
077	VVW	406	MW
079	VVW	408	W
07(11)	W	40(10)	M

TABLE II (contd.).

Prism Planes.

Indices.	Estimated Intensity.	Indices.	Estimated Intensity.
40(12)	W	110	S
50(11)	M	120	S
50(13)	W	210	MS
602	M	220	VW
606	VW	230	VS
608	VW	320	VS
60(10)	VVW	330	S
60(12)	MS	340	W
802	VW	440	MS

TABLE III.

General Planes.

Indices.	Estimated Intensity.	Indices.	Estimated Intensity.
111	VS	11(13)	W
112	S	11(15)	W
113	M	11(16)	W
114	S	11(17)	W
115	S	121	M
116	MS	122	W
117	MW	123	M
118	MW	124	S
119	VW	125	S
11(10)	MW	126	MS
11(11)	W	127	M
11(12)	W	129	VVW

TABLE III (contd.).

General Planes.

Indices.	Estimated Intensity.	Indices.	Estimated Intensity.
12(10)	VW	148	W
12(11)	W	149	W
12(12)	W	14(10)	VVW
12(13)	W	14(11)	W
12(14)	VW	14(12)	VW
12(15)	VW	14(13)	VW
12(16)	W	14(14)	W
12(17)	VVW	151	W
131	S	152	W
132	S	153	W
133	S	154	MS
134	W	155	W
135	S	157	W
136	S	158	M
137 ¹¹	VW	15(10)	VW
138 ¹⁴	W	15(14)	VW
139	W	161	MS
13(11)	VW	162	MW
13(12)	VW	163	W
13(13)	W	165	W
13(14)	W	166	MS
13(15)	VW	167	M
141	W	168	W
142	W	16(10)	VVW
143	S	16(11)	VVW
144	S	16(13)	W
145	MS	171	VW
146	MS	173	VW
147	M	174	VW

TABLE III (*contd.*).

General Planes.

Indices.	Estimated Intensity.	Estimated Intensity.
179	VW	VW
183	VW	M
184	VW	MS
186	VVW	W
189	VW	VVW
192	VVW	W
193	VW	W
194	W	W
195	W	VW
196	VVW	M
197	W	S
1 (10) 2	VW	W
1 (10) 3	VW	W
211	S	MS
212	VS	MS
213	VW	VW
214	MS	VW
216	MS	M
217	M	W
218	MS	VW
21 (10)	MW	MS
21 (13)	W	S
21 (14)	VW	W
21 (15)	VVW	MS
221	S	VW
222	VW	W
223	VS	MS
224	W	W
225	W	MS

TABLE III (contd.).

General Planes.

Indices.	Estimated Intensity.	Indices.	Estimated Intensity.
253	VW	335	W
311	MW	336	M
312	M	337	MS
313	W	338	VW
314	W	339	VW
315	MS	33(10)	VW
316	MS	33(11)	VW
317	W	33(12)	VW
318	VVW	341	W
31(10)	W	342	W
31(11)	MW	343	W
31(12)	VW	344	M
31(13)	VW	345	MW
31(14)	VW	346	VW
321	MW	347	VVW
322	VW	348	VVW
323	W	349	VW
324	MS	34(10)	VW
325	W	34(11)	VVW
326	MS	34(12)	VVW
327	W	351	VW
328	VVW	352	VW
329	VW	353	W
32(10)	VW	354	VW
32(12)	VW	357	VW
32(15)	W	358	VW
331	MS	359	VW
332	M	35(11)	VW
333	MS	35(12)	VW

TABLE III (*contd.*).

General Planes.

Indices	Estimated Intensity.	Indices.	Estimated Intensity.
360	MS	435	W
362	VW	436	VW
364	VW	439	VW
365	M	43(11)	VW
366	MS	446	VV
367	M	44(10)	MW
368	VW	511	MS
36(11)	VW	512	VVW
374	VW	514	W
377	VVW	515	W
383	VW	516	W
384	VW	517	VW
411	MW	51(10)	VW
412	W	51(12)	MW
413	MS	51(13)	VW
414	W	521	W
419	W	522	VW
41(12)	VVW	524	VW
41(13)	VW	525	VVW
41(15)	VW	526	MS
421	W	528	W
422	W	52(11)	VW
424	MS	52(13)	VVW
425	W	531	W
428	W	532	VVW
42(12)	VVW	534	VW
431	W	535	W
432	MW	537	W
433	MS	53(11)	W

TABLE III (contd.).

General Planes.

Indices.	Estimated Intensity	Indices.	Estimated Intensity
541	VW	633	MW
611	VVW	63(10)	W
613	W	641	VW
618	VW	713	VW
621	VVW	716	MW
622	MW	717	MW
624	W	718	MW
627	VVW	726	VW
629	VVW	736	VVW
631	VW		

From the measurements of the magnetic susceptibilities of this crystal J. Bhattacharjee² of this Laboratory comes to the conclusion that the plane of the benzene ring should be very nearly parallel to the 103 plane. From the space-group and the number of molecules per unit cell we see that the 001 plane must be a plane of symmetry or the normal to this plane should be an axis of symmetry. In the case of metadinitrobenzene,³ it has been found that the molecule has a plane of symmetry. This shows that substitutions in the meta positions are symmetrical with respect to a plane normal to the benzene ring and bisecting it. In the case of phloroglucine we may imagine a similar plane bisecting the benzene ring and containing one of the OH groups and from analogy with metadinitrobenzene this plane will be a plane of symmetry of the molecule. Since the benzene planes are nearly parallel to the (100) face, and due to the glide plane parallel to (010), we have a double layer of molecules of phloroglucine parallel to (100). The length of the a-axis is 6.80 Å, which is double the thickness of the benzene ring and hence it is not possible that the H₂O molecules lie between the phloroglucine planes; it is therefore, very natural that the H₂O molecules lie in the same planes as the phloroglucine molecules. The arrangement of the atoms parallel to the (100) face are shown in figure 1. The dotted lines show the positions of the atoms in a layer which is about 3.4 Å above the layer shown in continuous line.

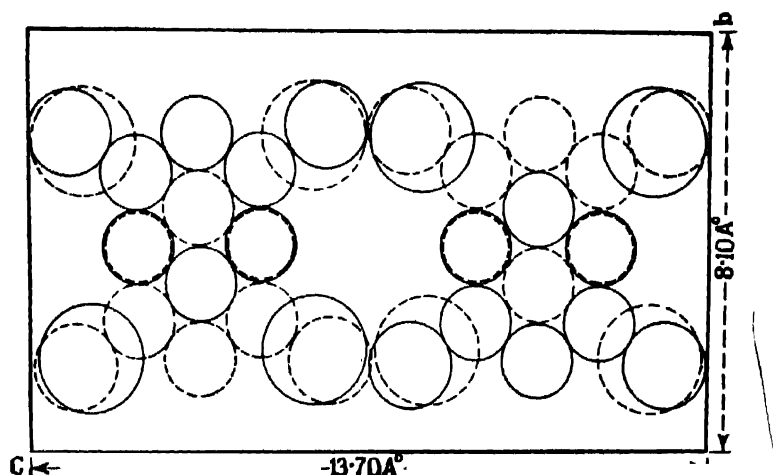


FIGURE 1.

The positions of the H_2O molecules are only tentative and are obtained only from considerations of the molecular dimensions and the size of the unit cell. As it has not been possible to get any idea about their orientation they are represented in the diagram as large circles, while the carbon atoms and the OH groups are represented by small and medium circles respectively.

REFERENCES

- ¹ Bernal, *Proc. Roy. Soc., A*, **113**, 117 (1926)
- ² Unpublished data.
- ³ Hertel, E. and Schneider, K., *Z. Phys. Chem., B*, **7**, 188 (1930).

ON THE ELECTRONIC CONDUCTION DUE TO 4f-ELECTRONS IN SOME TRIVALENT RARE-EARTH COMPOUNDS

By KRISHNAPADA GHOSH, M.Sc.

Lecturer in Physics, Scottish Church College, Calcutta

AND

BONBEHARI GHOSH, M.Sc.

(Received for publication, June 27, 1958.)

ABSTRACT. The conductivity of fluorides of La, Ce, Pr, and Nd in the form of fine crystals has been measured by compressing them to the form of solid rings placed between two co-axial cylindrical electrodes. Taking lanthanum fluoride as standard and subtracting the conductivity of lanthanum fluoride from those of other fluorides, the contribution to conductivity due to 4f-electrons has been determined. Using a formula similar to that of Wilson for semi-conductors, it is found that ΔH^* calculated from the measurements agrees approximately with the over-all width of the multiplet structure of the free ions of these elements as obtained from magnetic and spectroscopic data.

INTRODUCTION.

The phenomenon of conduction of electricity through solids (particularly through crystalline substances) has been subjected to many mathematical and experimental investigations during the past ten years and almost all the fundamental principles underlying the phenomenon appear to have been discovered. The case of a single crystal of simple structure is easily amenable to mathematical analysis. The mode of analysis consists in regarding a single crystal with its family of atoms and electrons as one dynamical system. The electrons belonging to this system are supposed to move in spatially periodic or quasi-periodic field of the lattice. This periodic field of the lattice is not permanent ; it is disturbed by the lattice vibrations resulting in scattering of the electrons. In the simplest case of stationary periodic field, Bloch¹ has shown that the energy of electrons in the lattice is divided into groups of levels separated by forbidden zones of disallowed energy in the space of reduced wave vectors or the k -space.

These groups of allowed energy bands in the k -space have been investigated by Brillouin² in crystals of various structures and are called the Brillouin-zones.

The distribution of electrons in these zones at the absolute zero follows the Fermi distribution law. At other temperatures the surface of Fermi distribution is not sharp. The electrons near the surface are regarded as free, and here the law of Maxwellian distribution is obeyed. It is the electrons which lie near the surface of Fermi distribution ($\partial f_0 / \partial E \neq 0$) that are responsible for conduction of electricity and these are called the conduction electrons.

In the case of a perfect and infinite crystal, an electron in one band can be excited to another level in a second allowed band of higher energy having the same value of the reduced wave vector; but in a small crystal this selection rule breaks down, so that the band structure becomes relatively unimportant. In the particular case when the surface of Fermi distribution occupies only a small volume of the Brillouin zone, the effect of the zone structure becomes small and Sommerfeld's picture³ of metallic conduction is very near the truth. But in the more general case the analysis becomes very complicated owing to the overlapping of the bands and it is difficult to obtain a quantitative estimation from purely mathematical considerations. When the surface of Fermi distribution comes very close to the boundary of the zone, the substance exhibits the characteristics of an insulator or of a semi-conductor. Strictly speaking there is no sharp line of demarcation between an insulator and a semi-conductor. It was suggested by Gudden⁴ that semi-conductors owe their conductivity to the presence of impurities.

Based on Gudden's idea, Wilson⁵ suggested a model for semi-conductors with simple cubic structure. Fowler⁶ presented Wilson's theory in a simplified form and applied it to three different models of semi-conductors. These three models are represented diagrammatically in Fig. 1.

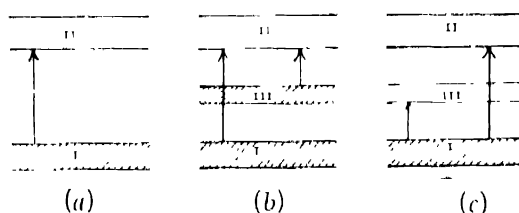
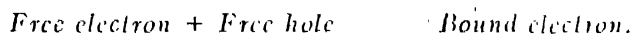


FIGURE 1.

Fig. 1 (a) shows the model of an *intrinsic* semi-conductor. Here the lower band (I) is completely full and the upper band (II) of higher energy is completely empty at the absolute zero of temperature. At ordinary temperatures, if the energy difference ΔE between the two bands be small compared to kT , some electrons from the top of the lower band (I) will make transition to band (II) leaving an equal number of positive "holes" in the band (I). These positive holes in band (I) and the electrons in the band (II) are free and obey Maxwellian

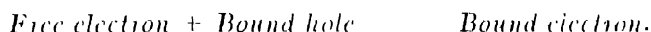
distribution. In the equilibrium state a law similar to that of dissociative equilibrium is obeyed :



Both the free electrons and free holes take part in conduction, the motion of positive holes in a given direction being equivalent to that of an electron in the opposite direction. It appears that the model of an insulator is similar to Fig. 1 (a) with the difference that ΔW in the case of an insulator is much larger than that of a semi-conductor (usually of the order of 2 volts). Thus conduction is impossible at ordinary temperatures. These insulators may, however, conduct electrolytically in which case heavier ions are deposited at the two electrodes and produce the effect of polarisation. This electrolytic conductivity is given by

$$\sigma = \sigma_0 e^{-\lambda/T}$$

The model of a normal *extrinsic semi-conductor* is shown in Fig. 1 (b). Here a completely filled impurity level (III) is present between the levels (I) and (II). In this case transition to (II) is possible both from the levels (I) and (III), the latter predominating at ordinary temperatures. Here the condition of equilibrium is



The case of an *abnormal extrinsic semi-conductor* is represented in Fig. 1 (c). Here the impurity level (III) is empty and again lies between (I) and (II). In this case electrons may be excited from (I) to both the levels (II) and (III).

In every case the conductivity of a semi-conductor at any temperature is given by an equation of the form

$$\sigma = \sigma_0 e^{-\Delta W/2kT} \quad (1)$$

where σ_0 is a constant which depends to a small extent on the temperature, but primarily on the structure of the crystal.

Purpose of the present investigation.—In the types of semi-conductors shown in Fig. 1 the lower band is completely filled up, and conduction is only possible by removal of an electron by thermal agitation to an upper band. Another class of semi-conductors is possible in which a valency shell of the positive ions is not completely filled up as in the *d*-shell of ions of the transition group of elements, and the *f*-shell of ions of the rare earth elements. The conductivity of the oxides of the iron group of elements has been the subject of a

large number of investigations. It has been found that the conductivity varies over a wide range, from $\log_{10}\sigma = 2$ for Fe_3O_4 to $\log_{10}\sigma = -7$ to -10 for oxides of Mn, Co, Ni, etc. Further, it is found that in the case of NiO, slight stoichiometric excess of the oxygen introduces a large change in the conductivity. In all these oxides, a partially filled up Brillouin zone exists and these semi-insulating properties (barring the case of Fe_3O_4) cannot be ordinarily understood unless it is assumed that the potential barrier between the ions of one kind (here the cations) is comparatively high and, therefore, the probability of interchange of electrons between them decreases rapidly. De Boer and Verwey⁷ have summarised the behaviour of this class of semi-conductors and have attempted to interpret them in terms of the presence of stoichiometric excess of one of the constituents of either the cation or the anion. With this class of semi-conductors it has not, therefore, been possible to associate the separation of the energy levels, found from the conductivity formula, with the multiplet separation of ground term of the cations.

In the present investigation we have considered the conductivity of salts of the rare earth elements, in which the partially filled up Brillouin zone is the $4f$ -shell, which, being inside the $5s^2p^6$ shell, is very little influenced by the external crystalline field, the splitting being of the order of 10^2 cm^{-1} . For this purpose we have taken the fluorides of La, Ce, Pr, and Nd, all of which have the same crystalline structure and belong to the hexagonal system. The nature of the crystalline field acting on the cation in all these crystals will, therefore, be the same. Further, the fluorides not being hygroscopic, the conductivity due to the absorption of water vapour may be made negligible by taking suitable precautions. The conductivity in this class of crystals is due to (i) the conductivity due to $4f$ -electrons which we shall denote by σ_f and (ii) that due to the remaining constituents of the crystals which we shall denote by σ_r ; this will include those due to the rest of the cation, the anion, and the extrinsic semi-conductivity of the crystal.

$$\text{Thus} \quad \sigma = \sigma_f + \sigma_r$$

We have made the assumption that since lanthanum fluoride has no electron in the f -shell of the cation, its conductivity $\sigma_{\text{La}} = \sigma_r$, and for the other crystals the "rest conductivity" at any temperature is the same as the conductivity of the LaF_3 crystal at that temperature. This assumes that all the crystals are of great purity and there is no variation in the extrinsic semi-conductivity in them.

Thus we have for any of the other crystals (say CeF_3)

$$\sigma_{\text{Ce}_f} = \sigma_{\text{Ce}} - \sigma_{\text{La}}$$

Having thus experimentally obtained values for the conductivity due to the presence of *4f*-electrons in crystals containing the ion Ce^{+++} , Pr^{+++} and Nd^{+++} , we have tried to see if the corresponding values of ΔW obtained from the conductivity formula could be correlated with the splitting of the ground term of these ions as obtained from optical and magnetic data. Some interesting results have been obtained which are reported in the present paper. The investigation is being continued to very low temperatures for which, owing to the extremely low values of the conductivity, more sensitive experimental arrangement is required.

PROCEDURE.

Preparation of compounds : As already mentioned, for our purpose anhydrous fluorides of rare earths lanthanum, cerium, praeosodymium, and neodymium were chosen. The fluorides of lanthanum and cerium were supplied by Messers. Riedel and Haen, in Germany and they bore the mark of purity. The fluorides of praeosodymium and neodymium were prepared from pure oxalate and sulphate of these elements in the chemical laboratory of the University College of Science under the supervision of Dr. P. B. Sarcar in the following way :

Praeosodymium oxalate was first converted into oxide by heating the oxalate at a temperature of about 800°C for several hours. The oxide was then converted into nitrate by treating it with concentrated nitric acid. The excess of nitric acid was removed by heating the nitrate solution in a water bath. The nitrate was next converted into fluoride by digesting it with concentrated hydrofluoric acid in a platinum basin placed on a water bath, when fine crystals of the fluoride were precipitated. The crystals were then washed thoroughly with hot water and then with alcohol and finally with 98% absolute alcohol. They were next covered with alcohol and heated in a water bath till they were completely dry. The crystals were afterwards placed inside an oven and heated to a temperature of 200°C for several days in vacuum.

To prepare neodymium fluoride, the neodymium sulphate was first converted into hydroxide by adding ammonium hydroxide. The hydroxide was then converted into nitrate and then into fluoride by the same method as described above for praeosodymium.

The prepared fluorides of praeosodymium and neodymium were analysed and were found to contain traces of oxyfluorides. Examined under microscope these compounds showed a crystalline structure.

Preparation of conductivity cells : To ensure good contact, brass cells with two co-axial cylindrical electrodes were preferred. The outer electrode was a hollow cylinder with thick walls ; the inner electrode was also a hollow cylinder provided with screw on its inner surface. For the sake of comparison four sets

of such inner and outer electrodes of exactly the same size were prepared from the same rod of brass. To minimise the effect of polarisation, the electrodes were platinised. One set of inner and outer electrodes was held in co-axial position by means of a slip-ring of hard steel fitting rather tightly within the space between the two electrodes and one of the fluorides was then introduced into the hollow thus produced. The other end of the hollow was then closed by a similar slip-ring (Fig. 2) and the fluoride was compressed to solid ring by means of hydraulic press. In this way four cells were prepared, all the fluorides being compressed to solid rings under the same pressure of 168 lbs. per sq. inch. To avoid contamination of surfaces of the compressed fluorides in contact with the slip rings during compression, the slip-rings were separated from the powder by means of mica-rings which (together with the slip-rings) were afterwards removed.

The prepared cells were then annealed for several days in vacuum at a temperature of about 200°C.

The apparatus: Since the resistance of these compounds is very high, extreme precaution was taken to avoid leakage. For this purpose the following arrangement of apparatus was found to be convenient. In Fig. 3, ABC is a copper tube sealed at the end C and provided with a screw near that end. The cells Ce, La, Nd and Pr were screwed to this end of the tube in the manner shown in Fig. 3. The copper tube with the cells was placed inside a wide pyrex tube about $3\frac{1}{2}$ ft. in length and provided with brass cap having ground conical joint. The open end A of the copper tube ABC was soldered to the upper cap. The leads from the outer electrodes were made to pass through four long side-tubes which were then sealed. The wide glass tube was provided with another side-tube by means of which it could be connected to a pump. To avoid any moisture leaking into the tube, a drying chamber was placed between the pump and the tube. The cells were dried and annealed inside the glass tube. In spite of all these precautions inconsistent results were obtained, particularly during the rainy season and this was due to leakage over the walls of the glass tube. This leakage was minimised by covering the walls of the tube with paraffin. The lower half of the apparatus was placed inside a Dewar's flask and maintained at constant temperatures. Since any trace of moisture absorbed by the fluorides produced an enormous increase in the conductivity, the prepared cells were thoroughly dried at 200°C for several days inside the glass-jacket maintained at a high vacuum. The measured conductivities given in table I are the conductivities of the dry fluorides in vacuum.

To measure the resistance of the cells, one terminal of a high-tension battery was connected permanently to the copper tube ABC (which served as the common lead to the inner electrodes) through a Hartmann Braun galvanometer of sensitivity equal to 4.63×10^{-10} amperes per millimetre at a distance of 116 cms. The other terminal of the battery was then placed successively in con-

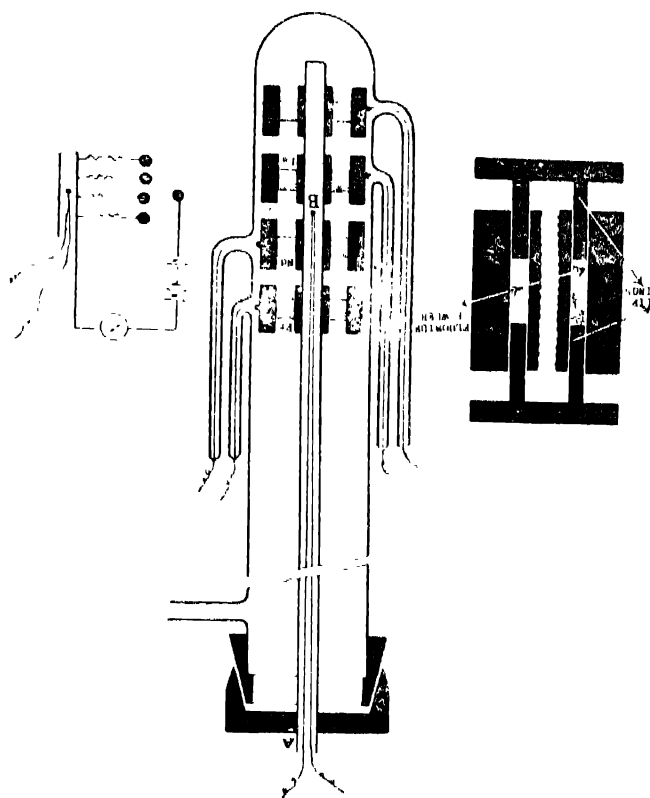


FIGURE 2.

FIGURE 3.

FIGURE 3(a).

tact with the leads to the outer electrodes connected to Ce, La, Nd, and Pr cells (Fig. 3a) and the corresponding deflections of the galvanometer were noted.

The temperature was measured by means of a copper-constantan thermo-couple, a Tinsley potentiometer being used for this purpose. One junction of the thermo-couple was placed inside the copper tube ABC, somewhere near the point B.

The effect of polarisation was very appreciable at high temperatures. But below the room temperature and in vacuum it was not detectable. Below the ice-temperature the resistance increased very rapidly. Hence with the limited sensitivity of the arrangement, the observation could not be carried beyond a small range of temperature.

EXPERIMENTAL RESULTS.

The outer radius of the inner cylinder	= 1.5 cms.
„ inner „ „ outer „	= 2.0 cms.

The thickness of the Lanthanum ring	= 1.205 cms.
" " " Cerium "	= 1.485 cms.
" " " Pracsodymium ring	= 0.606 cms.
" " " Neodymium "	= 0.586 cms.

The specific resistance was calculated from the relation⁸

$$\rho = \frac{2\pi KL}{\log_e(r_2/r_1)} \quad (2)$$

where

ρ = specific resistance,

K = total resistance measured,

L = thickness of rings of the compounds,

r_1 = inner radius of the ring,

and

r_2 = outer radius of the ring.

Substituting the value of $R = \frac{h}{k\theta}$

(where k is the galvanometer constant), the specific conductivity becomes

$$\sigma = \frac{k\theta \log_e(r_2/r_1)}{2\pi EL} \quad (3)$$

The result of the experiment is tabulated below :

TABLE I.

Temperature T in °K.	$\frac{1}{T} \times 10^3$	Specific conductivity $\times 10^{13}$			
		Lanthanum	Cerium	Pracsodymium.	Neodymium.
310	3225	1.881	69.42	32.97	20.05
308	3240	4.462	64.80	28.26	17.76
305	3278	3.068	47.26	20.78	12.61
298	3356	2.754	29.77	17.72	7.41
290	3378	2.492	29.23	14.86	7.00
281	3558	0.524	7.55	2.60	1.21
278	3597	0.439	6.37	2.35	0.99
261	3832	0.107	1.46	0.48	0.11

DISCUSSION OF EXPERIMENTAL RESULTS.

Fig. 4 shows that the specific conductivities of the fluorides plotted against reciprocal of absolute temperature gives an exponential curve, since the logarithm of conductivity similarly plotted gives a straight line (Fig. 5). Hence the conductivity at different temperatures must obey a relation of the form

$$\sigma = \sigma_0 e^{-\lambda/T} \quad \dots (1)$$

Since the measurements have been made on the crystal powders, the observed conductivity is the average over all directions in a single crystal.

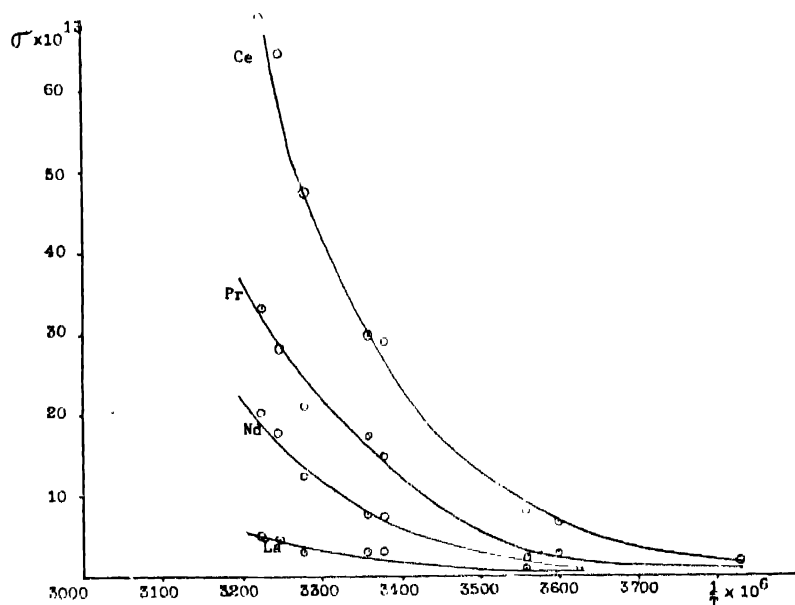


FIGURE 4.

Assuming that the average size of the grains is the same in these compounds, the difference in their conductivity may be attributed to the difference in their electronic configuration in the 4f-shell. This, according to Hund, is as follows :

At. No. of Ion.	Ion	No. of electrons in shells.			
		1,.....,43	44	51	52
54	La	Full	0	2	6
55	Ce	"	1	2	6
56	Pr	"	2	2	6
57	Nd	"	3	2	6

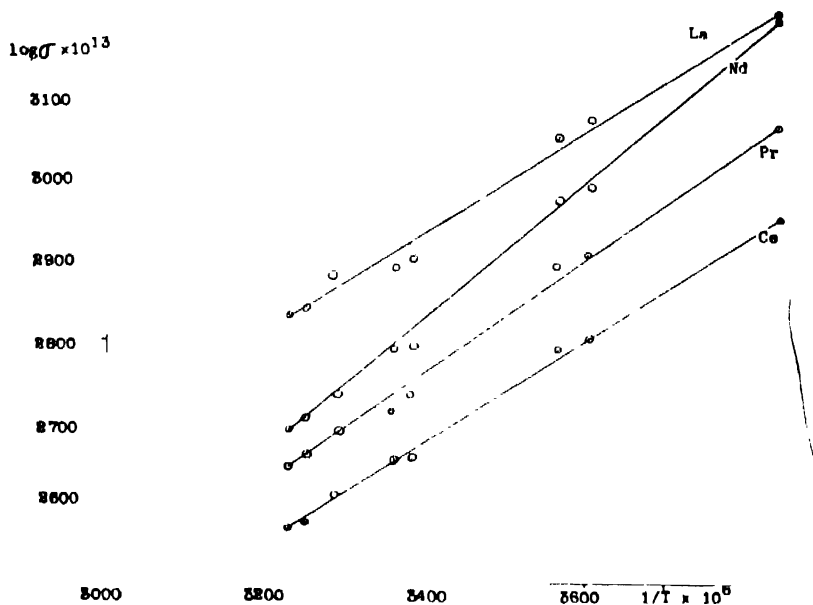


FIGURE 5.

Since we are concerned here only with the contribution to conductivity by the $4f$ -electrons, we represent (as mentioned above) the total observed conductivity σ_{Ce} (of cerium, say) as a sum of two conductivities $\sigma_{1.a}$ and σ_f where $\sigma_{1.a}$ is the "rest conductivity" and σ_f that due to the $4f$ -electrons.

Hence

$$\sigma_{Ce} = \sigma_{1.a} + \sigma_f \quad \dots (5)$$

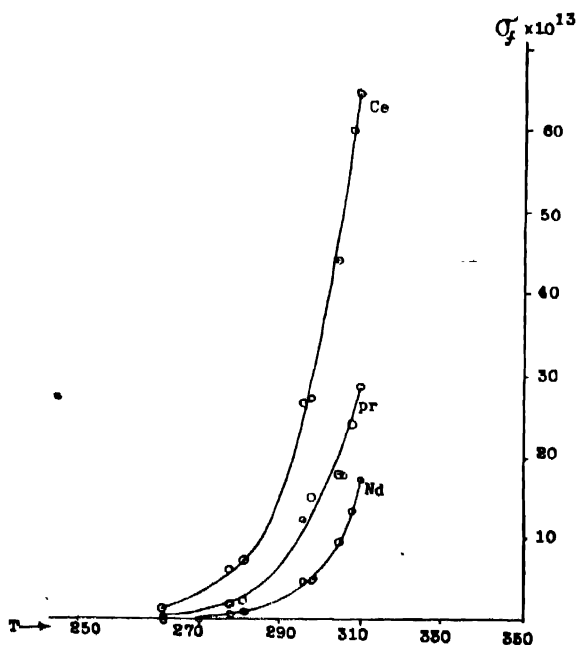


FIGURE 6.

In Fig. 6, σ_f has been plotted against absolute temperature. Within the small range of temperature employed the relation between σ_f and T seems to be an exponential one and the logarithm of σ_f plotted against $1/T$ again gives a straight line (Fig. 7).

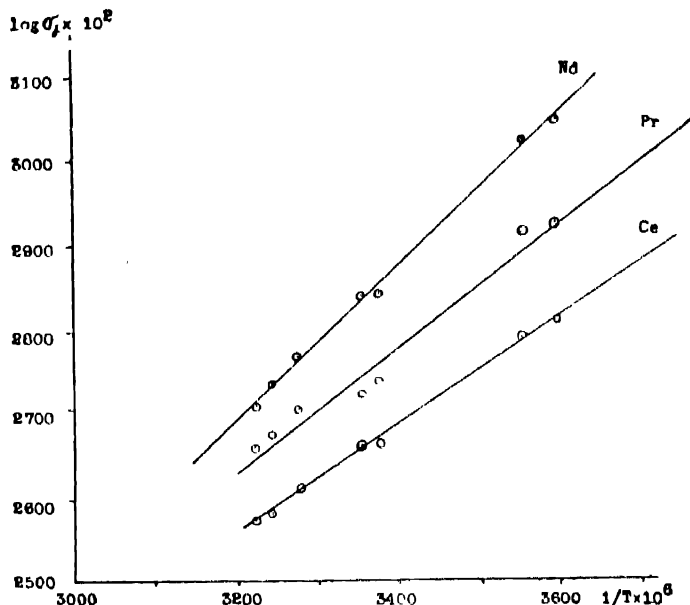


FIGURE 7.

Hence σ_f must be of the form

$$\sigma_f = \sigma_0 e^{-\lambda/T} \quad (6)$$

According to Wilson's model, the value of λ for semi-conductors is $\lambda = \frac{\Delta W}{2kT}$ where ΔW is the interval between the top of the completely filled band (I) and the bottom of the completely vacant band (II) as in (Fig. 1a), the numerical 2 in the denominator being due to the contribution by the free positive holes created in the band (I) by transfer of electrons from (I) to (II). In the case considered here the question of free positive holes does not arise and we can write

$$\sigma_f = \sigma_0 e^{-\Delta W/kT} \quad (7)$$

where σ_0 depends primarily on the number of free electrons taking part in conduction. Hence

$$\log \sigma_f = \log \sigma_0 - \frac{\Delta W}{kT} \quad (8)$$

It appears that the number of free electrons is, for the given range, independent of temperature. Plotting $\log \sigma_f$ against $1/T$, the value of ΔW can be calculated from the slope of the curve. According to Matthiessen's rule the value of ΔW thus calculated will not depend on the small quantity of impurity that might be present in the compounds. It will be found from table II that the value of ΔW obtained from our measurements agrees approximately with the over-all width of multiplet structure of ions of rare-earths under investigation as calculated from the magnetic and optical data.

TABLE II.

Ions.	ΔW (in electron volts)	
	Observed.	Calculated. ⁽⁹⁾
Ce	0.550	0.310
Pr	0.653	0.569
Nd	0.802	0.799

It will be seen that while the agreement between observed and calculated values of ΔW for praeodymium and neodymium is quite good; the observed value for Ce^{+4} is nearly double that of the calculated value.

It may be expected that measurements of conductivity of single crystals of similar structure and composition of these rare-earth elements may lead to independent evidence regarding the multiplet structure and their separation in the crystalline field. We are extending our observation in that direction.

This investigation was suggested to us by Prof. D. M. Bose, to whom our sincere thanks are due for granting us facilities to carry it out and for helpful discussions.

REFERENCES

- ¹ *Zeit. f. Physik*, **52**, 555 (1928).
- ² *Die Quantenstatistik*, Berlin (1931).
- ³ *Zeit. f. Physik*, **47**, 1 (1928).
- ⁴ *Erlangen Ber.*, **62**, 280 (1930).
- ⁵ *Proc. Roy. Soc.*, **134**, 277 (1931).
- ⁶ *Proc. Roy. Soc.*, **140**, 505 (1933).
- ⁷ *Proc. Phys. Soc. Lond.*, **49** extra, 59 (1937).
- ⁸ *Dictionary of Applied Physics* (Glazebrook), Vol. II, p. 686.
- ⁹ (Van Vleck - *Electric and Magnetic Susceptibilities*, p. 246
(Jackson—*Low Temperature Physics*, p. 106,

ON THE RAMAN SPECTRUM OF DIPHENYL

By S. K. MUKERJI, M.Sc., Ph.D. (LOND.)

Professor of Physics, Agra College, Agra

AND

S. ABDUL AZIZ, M.Sc.

Agra University Research Scholar in Physics

(Received for publication, May 25, 1938.)

Plate VII.

ABSTRACT. The Raman spectrum of molten diphenyl has been studied carefully with a view to record and assign correctly the faint Raman lines. A few new lines not observed by previous workers have been recorded by carefully suppressing the continuous background with the help of suitable filters. It is pointed out that most of the ground frequencies of benzene are also observed in the case of diphenyl and that the characteristic frequency due to the C—C binding between the two benzene nuclei is 1283 cm.^{-1}

INTRODUCTION

The Raman spectrum of diphenyl was studied formerly by Dadiou and Kohlrausch,¹ Wood,² and Donzelot and Chaix.³ There seems to be some discrepancy between the results obtained by the different authors and also the Raman spectrum recorded by them seems to be incomplete owing probably to the presence of a strong continuous background. An attempt has therefore been made in the present investigation to record the faint Raman lines due to this substance by using suitable filters in order to suppress the continuous background and to assign these lines correctly.

EXPERIMENTAL

Diphenyl obtained from the research laboratory of Eastman Kodak Company was further purified by repeated distillation, and the middle portion of the distillate was used, special care being taken to make the molten substance dust-free. The Wood's tube containing diphenyl was kept in a specially constructed small oven. As this substance was studied in the molten state so

this oven was heated electrically to a temperature slightly above the fusion point. A minute pointed gas flame was also placed a few centimetres below the horn of the Wood's tube projecting outside the oven to maintain the fluid inside just above the flame in the molten state. The slit of the spectrograph was kept very narrow in order to obtain the maximum resolution. Ilford Golden Isozenith plates, speed H and D. 1400 and also Agfa Isochrome backed plates H and D. 4400, were used for photographing the scattered spectra. The Golden Isozenith plates were also backed before use to eliminate the halation accompanying the strong lines. Exposures varying from eighty to over one hundred hours were found necessary to bring out the fainter lines. The source of light was a quartz mercury-vapour lamp and the spectrograms were obtained with a Hilger's quartz H_2 spectrograph and also with a fairly rapid Fuess glass spectrograph, having a dispersion of about $21\text{\AA}$ per mm. in the region of $4358\text{\AA}$. Special care was taken to shield all extraneous light by suitable screens and apertures, and the genuinely scattered light was focussed on to the slit of the spectrograph. The plates were measured on a fairly accurate photomeasuring micrometer. The wave lengths were calculated using the well-known Hartmann's dispersion formula. For comparison and checking the results the spectrum of an iron arc was also used.

In this investigation two photographs were taken, one with a solution of sodium nitrate of suitable concentration as a filter to cut off the light of the $4046\text{\AA}$ group of lines of the mercury arc so that only the $4358.8\text{\AA}$ mercury line was used as the exciting line. This photograph under such an excitation was found to be remarkably free from the continuous fluorescent background mentioned before. The other photograph was taken with a very dilute solution of sodium nitrate filter to weaken the $3650\text{\AA}$ mercury line. It was followed by a filter of a very dilute solution of iodine in carbon tetrachloride to remove the continuous background in the region between $4358\text{\AA}$ and $4046\text{\AA}$. In this case the excitation was by both λ_{4358} and λ_{4046} . This photograph was taken to verify the lines obtained by λ_{4358} excitation but it gave some fluorescence due to also $4046\text{\AA}$ excitation. In addition to the new lines obtained, this investigation has given all the lines obtained by Donzelot and Chaix. The spectrograms are reproduced in plate VII.

The results are given in tables I and II. Complete tables showing also assignments are given at the end of the paper.

The results obtained by Wood and by Donzelot and Chaix have also been tabulated in table III, along with those of the authors for a comparative study.

It is evident that all the frequencies given in table I are due to $4358\text{\AA}$ excitation. In addition to these, the wave-numbers of the anti-Stokes lines obtained due to this excitation are 23941, 23678, 23552, 23346, 23251, and 23205.

TABLE I.

Diphenyl Frequencies.

(With a filter of concentrated solution of sodium nitrite.)

Number.	$\Delta\nu$ in cm. ⁻¹	Intensity I.	Number.	$\Delta\nu$ in cm. ⁻¹	Intensity I.
1	3192	0	17	1002	10
2	3062	5	18	980	1
3	3047	1	19	991	1
4	2991	0	20	867	(1/2)
5	1610	10	21	838	4 (Broad)
6	1590	8	22	779	1
7	1506	4	23	749	5
8	1452	1	24	614	4
9	1376	0	25	518	1
10	1318	(1/2)	26	449	0
11	1283	10	27	408	5 (Broad)
12	1241	1	28	368	0
13	1189	3	29	313	4 (Broad)
14	1157	4	30	267	4 (Broad)
15	1090	(1/2)	31	194	0
16	1032	5	32	140	4 (Broad)

TABLE II.

Diphenyl Frequencies.

(With a filter of a very dilute solution of sodium nitrite followed by a filter of a dilute solution of iodine in carbontetrachloride.)

Number.	Assignment.	$\Delta\nu$ in cm. ⁻¹	Intensity.	Number.	Assignment	$\Delta\nu$ in cm. ⁻¹	Intensity.
1	A	3192	0	4	A	2991	0
2	A	3062	5	5	A	1610	10
3	A	3047	1	6	A	1590	8

TABLE II (contd.).

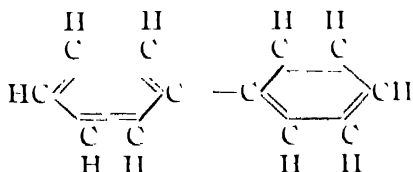
Diphenyl Frequencies.

(With a filter of a very dilute solution of sodium nitrite followed by a filter of a dilute solution of iodine in carbontetrachloride.)

Number	Assignment	ν , in cm^{-1}	Intensity	Number	Assignment	$\Delta\nu$ in cm^{-1}	Intensity
7	A	1500	4	31	B	1500	1
8	A	1452	1	35	A	1267	1 (broad)
9	B	1400	3	36	B	1452	1
10	A	1318	0	37	B	1370	2
11	A	1283	10	38	A	+1408	1 (broad)
12	B	1247	2	39	B	1283	10
13	A	1211	1	40	B	1241	1
14	A	1180	3	41	B	1180	2
15	A	1157	1	42	B	1157	1
16	A	1090	0	43	B	1090	0
17	A	1032	5	44	B	1030	5
18	A	1003	10	45	B	1003	10
19	A	980	1	46	B	980	1
20	A	961	1	47	B	961	2
21	A	898	1	48	B	898	0
22	A	838	3 (broad)	49	B	838	3 (broad)
23	A	770	1	50	B	770	3
24	A	740	5	51	A	+1003	1
25	A	614	4	52	B	740	5
26	A	548	1	53	B	614	4
27	A	419	0	54	B	408	4 (broad)
28	A	408	1 (broad)	55	B	313	3 (")
29	A	313	3 (")	56	B	267	4 (")
30	A	267	4 (")	57	B	140	4 (")
31	A	140	1	58	B	+140	2 (")
32	B	1010	10	59	B	+267	1 (")
33	B	1090	8	60	B	+313	1 (")

DISCUSSION OF RESULTS

Diphenyl, $C_{12}H_{10}$, consists of two benzene nuclei joined end on by C—C bond in the para-direction. It was expected, therefore, as has been observed by Wood (*loc. cit*), that most of the fundamental frequencies of benzene will also be represented by diphenyl. Of the seven Raman active modes of vibration of benzene worked out by H. B. Wilson,⁴ which are considered to be the funda-



mental modes of vibration, all have been observed to be present in diphenyl. The line at frequency 3170 cm^{-1} has been observed and recorded by Wood as a fairly strong line but it does not appear at all on any of our plates. Nor have Donzelot and Chaix recorded it. A very faint line has, however, been obtained by us at a frequency 3192 cm^{-1} , due to only $4358\text{\AA}$ excitation. The line $\lambda 4673$ recorded by Wood at 1544 cm^{-1} appears as a double line on our plate at frequencies 1610 and 1590 cm^{-1} respectively, excited by both $4358\text{\AA}$ and $4347\text{\AA}$. Their intensities are 10 and 8 when excited by $4358\text{\AA}$ and 2 and 1 when excited by $4347\text{\AA}$. As the frequency shifts come out to be the same, 1610 and 1590 cm^{-1} due to both the above-mentioned excitations with the corresponding intensities noted above it is quite clear that these two frequencies are real and there is no line at 1544 cm^{-1} . Moreover, the frequency 1544 cm^{-1} recorded by Wood is not verified in this investigation by $4046\text{\AA}$ excitation. The line at 1178 cm^{-1} of benzene appears in diphenyl, as will be seen in table I, as a doublet with two components at 1189 and 1157 cm^{-1} respectively. Besides the frequencies which are characteristic of the benzene nucleus diphenyl gives as will be seen in table I, some fairly intense lines at 1506 , 1283 , 740 , 313 , 267 and 140 cm^{-1} , respectively. Among these frequencies the one at 1283 cm^{-1} has been found to be the most prominent. It is not represented in benzene. It is also absent in the infra-red spectrum of benzene. Ananthakrishnan⁵ working with a high dispersion spectrograph of special design, in his recent paper on the Raman spectrum of benzene has not recorded it. Grassmann and Weiler⁶ have, however, reported a very faint line due to benzene at 1283 (o). But intensity considerations show that 1285 (10) of diphenyl and 1285 (o) of benzene have different origins.

TABLE III

Number	Mukerji and Abdul Aziz.	Wood.	Donzelot and Chaix.
1	3102	—	—
2	—	3170	—
3	3062	3055	3055
4	3047	—	—
5	3061	—	—
6	1610	1603	1600
7	1590	1584	1589
8	—	1544	—
9	1506	—	1503
10	1452	—	—
11	1376	—	—
12	1318	—	—
13	1283	1280	1281
14	1241	—	—
15	1189	1191	1187
16	1157	1146	1150
17	1090	—	—
18	1032	1023	1029
19	1003	990	1001
20	980	—	—
21	964	—	—
22	898	—	—
23	838	810	834
24	779	766	776
25	740	731	739
26	614	606	611
27	548	—	—
28	449	—	—
29	408	416	405

TABLE III (contd.).

Number.	Mukerji and Abdul Aziz	Wood.	Donzelot and Chaix.
30	368	-	-
31	313	-	316
32	267	-	267
33	193	-	-
34	140	-	141

This line is also absent in the Raman spectrum of diphenyl oxide. Hence it is evident that the C-C binding between the two benzene nuclei is responsible for the origin of this line. The frequency usually observed for C-C vibration lies in the neighbourhood of 1000 cm.^{-1} . As in this case the two carbon atoms are joined to heavy nuclei so the effective force for the C-C vibration may be expected to be greater and therefore, it may be argued, that this increased frequency 1283 is obtained. This illustrates the point as argued by D.H. Andrews⁷ that a frequency depending principally on the nature of the bond is affected substantially by the nature of the rest of the molecule. In the case of $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$, for example, the frequency corresponding to $\text{C}\equiv\text{C}$ rises because of the fact that one of the vibrating carbon atoms is joined to a heavy benzene nucleus. When the other hydrogen atom is again replaced by a heavy group, the frequency rises still more. Thus in the case of $\text{C}_6\text{H}_5\cdot\text{C}\equiv\text{C}\cdot\text{C}_2\text{H}_5$, the frequencies observed corresponding to $\text{C}\equiv\text{C}$ vibrations are 2210 and 2238 cm.^{-1} . Arguing in this way it can also be suggested that in the case of diphenyl the effective force of vibration for C-C bond is very much increased because of the fact that both carbon atoms are parts of the two heavy nuclei.

Also it has been shown by Dhar⁸ that the distance between the two C-C atoms is 1.48, *i.e.*, slightly less than the actual distance for the aliphatic linkage. This shows that the binding is slightly stronger than the aliphatic C-C binding.

It might be interesting to note here that just before communicating this paper we obtained a large number of Raman lines for the first time due to *o*-diphenyl benzene. This substance consists of three benzene nuclei instead of two, two of these being substituted in the third in the ortho position. A large number of these new frequencies obtained by us have been found to agree remarkably well with those due to diphenyl. As obtained in diphenyl, the strongest Raman frequency given by this substance is at 1288 cm.^{-1} . Details of this investigation will be communicated later.

TABLE IV.

Exciting Lines.

Exciting Line A.	Notation.	Wave-number cm^{-1}
4358.3	A	22938
4347.8	A_1	22905
4330.2	A_2	23039
4165.1	B_2	24335
4077.8	B_1	24510
4046.6	B	24705

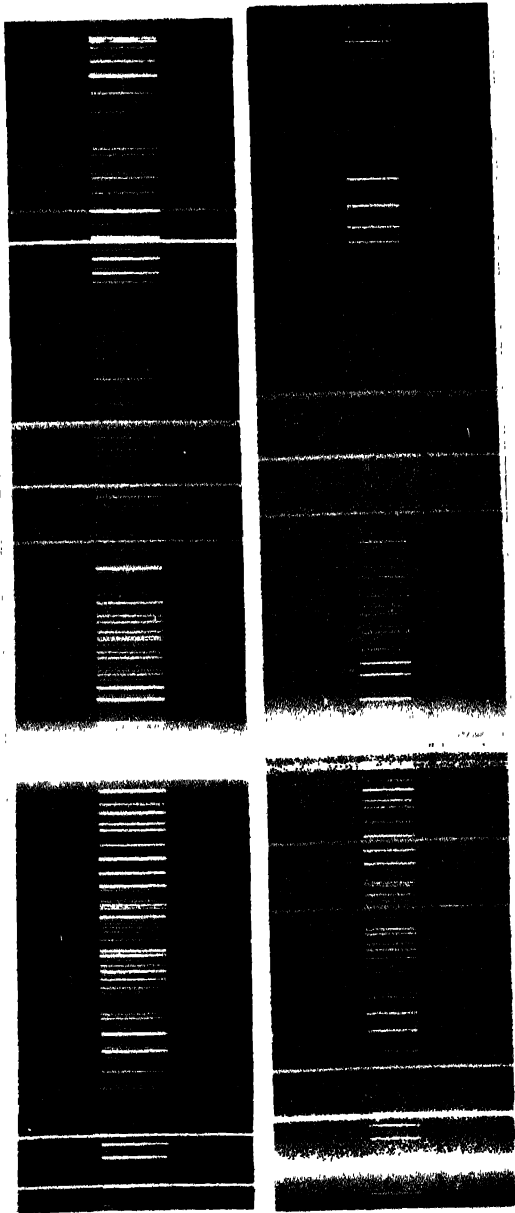
TABLE V.

Diphenyl frequencies with a concentrated solution of sodium nitrite filter.
Excitation by λ_{4358} group only.

Number	Wave-number	Intensity	Assignment	Shift cm^{-1} $\Delta\nu$
1	10710	6	A	3102
2	10876	5	A	3062
3	10891	1	A	3047
4	10032	6	A_1	3063
5	10077	6	A	2961
6	21328	10	A	1610
7	21348	8	A	1590
8	21386	2	A_1	1609
9	21405	1	A_1	1590
10	21432	4	A_1 } A_2 }	1506 1607
11	21485	1	A	1453
12	21558	6	A	1380
13	21620	3	A	1318
14	21655	10	A	1283
15	21695	1	A	1243
16	21715	2	A_1	1286

116 4328 A

116 4047 A



(a)

(b)

Raman spectrum of diphenyl—

- (a) With a filter of conc. solution of NaNO_2
- (b) With a filter of conc. solution of NaNO_2 and another of iodine in CCl_4

TABLE V (contd.).

Number.	Wave-number cm^{-1} ν .	Intensity	Assignment.	Shift cm^{-1} $\Delta\nu$.
17	21752	3	Λ_1 }	1186
18	21781	4	Λ_2 }	1287
19	21848	$\frac{1}{2}$	Λ	1099
20	21907	5	Λ	1031
21	21935	10	Λ	1003
22	21958	1	Λ	980
23	21976	1	Λ	962
24	21993	2	Λ_1	1002
25	22038	1	Λ_1 }	900
26	22100	4	Λ_2 }	1001
27	22159	4	Λ	838
28	22199	5	Λ_1 }	779
29	22254	$\frac{1}{2}$	Λ	836
30	22325	4	Λ	739
31	22390	1	Λ_1	741
32	22491	0	Λ	613
33	22530	5 br.	Λ	548
34	22570	0	Λ	447
35	22584	0	Λ	408
36	22625	4 br.	Λ_1	368
37	22671	4 br.	Λ	411
38	22726	0	Λ	313
39	22745	0	Λ_1	267
40	22798	4 br.	Λ	269
41	23205	2 br.	Λ	193
42	23251	1 br.	Λ	140
43	23346	2 br.	Λ	267
44	23552	1	Λ	313
45	23679	0	Λ	408
46	23943	2	Λ	614
47	24219	0	Λ	741
				1005
				1281

TABLE VI.

Diphenyl frequencies with very dilute filters of sodium nitrite, and of iodine in carbon tetrachloride. Excitation by both λ_{4358} and λ_{4047} groups.

Number.	Wave-number ν .	Intensity.	Assignment.	Shift cm.^{-1} $\Delta\nu$.
1	19746	0	A	3102
2	19877	5	A	3061
3	19893	1	A	3045
4	19933	0	A ₁	3062
5	19977	0	A	2961
6	21328	10	A	1610
7	21347	8	A	1591
8	21387	2	A ₁	1608
9	21404	1	A ₁	1591
10	21431	4	A } A ₂ }	1507 1608
11	21453	1	B ₁	3063
12	21485	1	A	1453
13	21620	0	A	1318
14	21643	3	B	3062
15	21656	10	A } B }	1282 3049
16	21696	1	A	1242
17	21714	2	A ₁	1281
18	21752	3	A } A ₂ }	1186 1287
19	21780	4	A	1158
20	21849	0	A	1089
21	21905	5	A	1033
22	21935	10	A	1003
23	21959	$\frac{1}{2}$	A	979
24	21977	$\frac{1}{2}$	A	961
25	21994	2	A ₁	1001
26	22036	1	A } A ₂ }	902 1003
27	22099	3 br.	A	839
28	22158	4	A } A ₁ }	780 837

TABLE VI (contd.).

Number.	Wave-number cm.^{-1} ν .	Intensity.	Assignment.	Shift cm.^{-1} $\Delta\nu$.
29	22196	5 br.	A	712
30	22254	0	A ₁	744
31	22344	4	A	614
32	22390	1	A	518
33	22486	0	A	452
34	22530	4 br.	A	408
35	22584	0	A ₁	411
36	22626	3 br.	A	312
37	22672	4 br.	A	266
38	22709	4 br.	A	139
39	23005	10	B	1610
40	23115	8	B	1590
41	23200	4	B	1505
42	23206	1	A	268
43	23232	4	B ₁	1281
44	23255	1	B	1450
45	23332	0	B } B ₂ }	1373 1003
46	23346	1	A	408
47	23422	10	B	1283
48	23466	1	B	1239
49	23482	1	B ₁	1034
50	23513	5	B } B ₁ }	1192 1003
51	23548	4	B	1157
52	23613	0	B	1092
53	23674	5	B	1031
54	23702	10	B	1003
55	23725	1	B	980

TABLE VI (contd.).

Number.	Wave-number cm^{-1} ν .	Intensity.	Assignment.	Shift cm^{-1} $\Delta\nu$
56	23739	1	B B ₁ }	966 777
57	23777	1	B ₂ ⁺	739
58	23810	0	B	895
59	23867	3 br.	B	838
60	23900	1	B ₁	616
61	23926	3	B	779
62	23940	1	A	1002
63	23964	5	B	741
64	24091	4	B	614
65	24247	1	B ₁	269
66	24296	4 br.	B	409
67	24391	3 br.	B	314
68	24437	4 br.	B	268
69	24565	4 br.	B	140
70	24843	2 br.	B	138
71	24973	1 br.	B	268
72	25021	1 br.	B	316

br. indicates a broad line. A bar over the lines denotes anti-Stokes shifts.

REFERENCES.

- ¹ Dadiou and Kohlrausch, *Sitzber. Akad. Wiss. Wien, Abt. II a*, **138**, 799 (1929).
- ² Wood, *Phys. Rev.*, **36**, 1431 (1930); **38**, 2168 (1931).
- ³ Donzelot and Chaix, *Compt. rend.*, **201**, 501 (1933).
- ⁴ R. B. Wilson, *Phys. Rev.*, **45**, 706 (1934).
- ⁵ Ananthakrishnan, *Proc. Ind. Acad. Sci., A*, **4**, 52 (1936).
- ⁶ Grassman and Weiler, *Z. f. Phys.*, **86**, 321 (1933).
- ⁷ Andrews, *Phys. Rev.*, **36**, 541 (1930).
- ⁸ Dhar, *Ind. J. Phys.*, **7**, 43 (1932).

DIELECTRIC PROPERTIES OF SOME ORGANIC SUBSTANCES

By G. R. PARANJPE

AND

D. J. DAVAR

(From the Physics Laboratory, Royal Institute of Science, Bombay)

(Received for publication, July 12, 1938.)

ABSTRACT. The density, the refractive index and the dielectric constant are determined at room temperature (30°C) for the solutions of oleic acid, linolic acid, triolein, triricinolein, and tristearin, in benzene. The dielectric constant is determined at 7,500 Kc (40 meters) using the method of resonance and a valve-voltmeter. The refractive index is determined for Na lines. The polarizations and the electric moment of the substances are calculated from the Debye equation using the method of least squares. The electric moment is explained from the point of view of the chemical constitution and structure of the substances. The values obtained are: oleic acid 1.009, linolic acid 1.208; triolein 3.158, triricinolein 4.117 and tristearin 2.844.

The organic substances selected for the study of their dielectric properties at room temperature are (a) oleic acid, (b) linolic acid, (c) triolein, (d) triricinolein and (e) tristearin. All these are liquids at room temperature except tristearin which is a solid. An extra-pure variety of each of these substances was obtained from Messrs. Schering-Kahlbaum. An agreement of the physical constants as determined with those found in standard literature was taken to indicate purity and further purifications were not carried out. All the investigations were carried out at room temperature which was 30°C for oleic acid, linolic acid, and triolein, and 29°C for triricinolein and tristearin. Table I gives composite data regarding the substances.

TABLE I.

Substance.	Density.	Refractive index.	Dielectric constant.
Oleic Acid	0.8864	1.4571	2.414
Linolic Acid	0.9075	1.4718	2.675
Triolein	0.9134	1.4659	3.375
Triricinolein	0.9618	1.4763	
Benzene (solvent)	0.8674	1.4935	

The non-polar solvent benzene used for all the substances was obtained from Messrs. Schering-Kahlbaum and was guaranteed to be free from thiophene.

Standard 100 c.c. flasks equipped with tight-fitting stoppers were used for the preparation of the solutions. The concentration of the solution (in Mole fractions) was thus obtained by actual weighings. The density, the refractive index and the dielectric constant were then determined using the same solution. This procedure, though it involved a large quantity of the substances, was preferred on account of its independence of any graphical interpolations. The densities were determined by specific gravity bottles. On account of the high coefficient of expansion of benzene direct hand-contact with the specific gravity bottles was avoided. Some time was always allowed before weighing the bottle in order to allow it to come to room temperature. A correction for the quantity of benzene evaporating during this interval was made by determining the diameters of the capillary bore and noting the height of the solution in the capillary. The refractive index was determined for Na lines using the Abbe auto-collimating refractometer.

The dielectric constants were determined at 40 metres (7,500 Kc) using the comparison method of Hartshorn and Oliver¹ and taking benzene as the standard of reference. A simple one-valve oscillator (Hartley circuit) was used for generating the high frequency oscillations. It had an output of about 2 watts and in order to ensure the stability the valve was maintained entirely on independent batteries. The oscillator showed great stability at certain frequencies. From these a frequency 7,500 Kc was selected. This frequency was checked from time to time.

The oscillator, the receiver, the valve-voltmeter and the measuring condenser were very nearly the same as those described by Paranjpe and Deshpande.²

The receiving circuit consisted of a plug-in type inductance made of a few turns of silk covered thick copper wire in parallel with a standard condenser. The condenser was a precision type standard variable condenser manufactured by the General Radio Company. Its total capacity was $1,500 \mu\mu\text{F}$. A micrometer scale fitted to it enabled a reading of $0.95 \mu\mu\text{F}$ to be taken with ease. The backlash was found to be less than half a division on the micrometer scale. By taking readings in the same directions even this backlash was avoided. The instrument is enclosed in a dust-proof case which carries its own shield. The rotor terminal is fixed on the shield and is earthed. The operating handle is of rubber.

A valve-voltmeter was used for detecting the current in the receiving circuit. It offers a very sensitive means of indicating resonance and absorbs practically no power from the circuit. It has been used by Sudgen³ and Allen Astin⁴ who found it to be the most sensitive resonance indicator. The

circuit of the valve-voltmeter was that recommended by F. M. Colebrook.⁵ As designed, the full scale of the anode micro-ammeter is available for the measurement of the increase in the anode current due to the rectification of the applied alternating voltage. This arrangement gave ample sensitivity as an applied grid potential of 0.85 volt gave a full scale deflection of the micro-ammeter. A lamp-and-scale arrangement further magnified the deflection. In order to avoid any direct interaction between the oscillator and the valve voltmeter a distance of about 5 metres was kept between them.

The test condenser consisted of a Dewar's flask cut at its base and inverted. Two thick (0.45 mm.) silver plates bent cylindrically were fixed between the two walls of the flask. The plates were kept in position by the forces due to their elasticity and the use of solid supports was avoided. The plates were so made that when they were inserted into the Dewar's flask their curvature corresponded as nearly as possible to that of the walls of the flask. It was also seen that they formed complete cylinders when in position in the condenser, since an opening in the outer plate would lead to a considerable amount of error in the capacity measured. Leads were joined to small extensions of the silver plates which were bent at right angles. Baser materials were thus prevented from coming in contact with the liquid under investigation.

In order to have the geometrical configuration of the plates the same for the 'air capacity' and the 'liquid capacity,' the latter was determined by filling the condenser in position. The air capacity of the condenser was 30 $\mu\mu\text{F}$ while the fluid contents was 60 c.c. The air gap between the plates was 0.5 cm. The outer cylinder of the condenser was earthed which provided an almost complete screen. The test condenser was further completely screened and the screen was earthed.

RESULTS AND DISCUSSION.

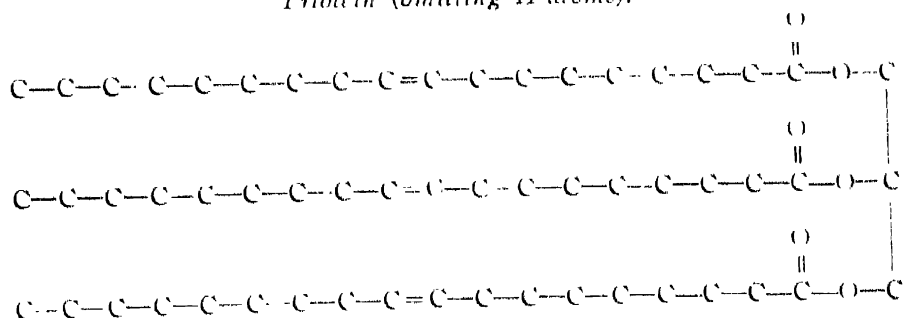
Table II gives the final results of these experiments :—

TABLE II.

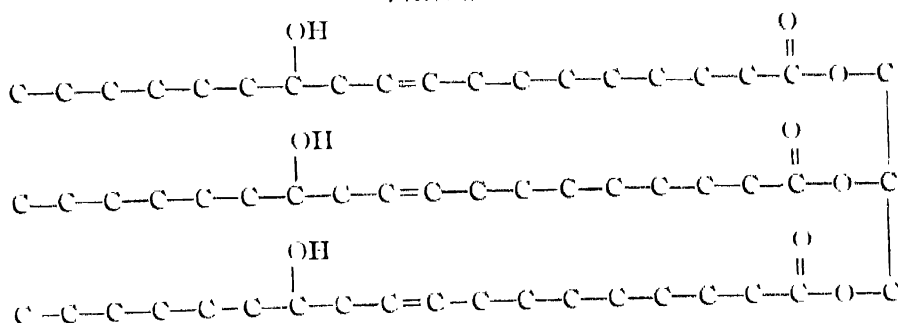
	Oleic acid	Linolic acid.	Triolein.	Trilin-olein.	Tri-stearin.
Molar polarization P_2 ...	104.770	114.073	459.612	619.013	430.376
Electronic Polarization P_{E_e}	84.052	84.356	265.639	272.735	265.023
Orientation Polarization P_μ	20.718	29.717	193.973	346.278	165.353
Electric Moment ...	1.009	1.268	3.158	4.117	2.844

The molecular polarization P_{12} of the mixture was calculated from the Debye equation

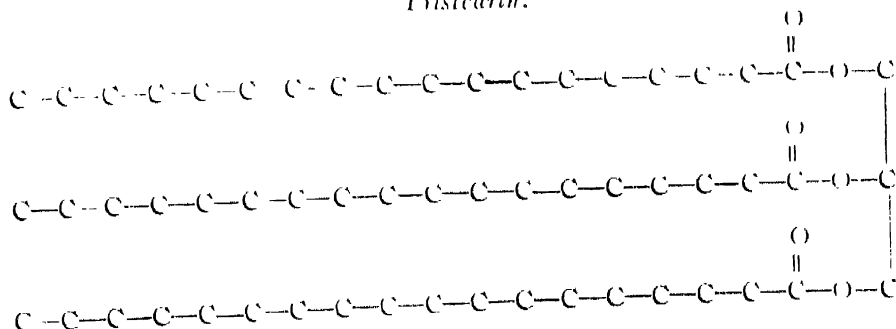
Triolein (omitting H-atoms).



Tricinolein.



Tristearin.



Comparing now oleic acid and linolic acid it may be observed that both have almost the same length of the carbon chain and a similar structure ; but while oleic acid has one double bond linolic acid has two. Smyth and Zaim⁶ have found that a small but definite moment is associated with a double bond. This leads us to expect a slightly larger value for the moment of linolic acid than of oleic acid. The experimental values 1.009 for oleic acid and 1.208 for linolic acid indicate a similar behaviour.

It may be noted that wherever the structures are similar the electronic polarizations are comparable (table II). Comparing oelic acid and linolic acid and triolein and tristearin it appears that the existence of a double bond has but little effect on the magnitude of the electronic polarization. Comparing

triricinolein with triolein and tristearin it appears that the field of the OH group is intense enough to cause not only a marked increase in the orientation polarization but also a noted rise in the electronic polarization.

According to Müller and Sack⁷ a long chain acetate molecule such as amyl has a moment 1.9. In the present case, however, the long chain molecules of the acids have a much smaller moment in spite of the existence of double bonds.

It may be expected that a triglyceride, since it has three times as long a chain as the acid from which it is derived, may possess an electric moment three times that of the acid. The data for oleic acid and triolein (table II) agree favourably with this view.

Comparing the three triglycerides the electric moment increases in the order tristearin, triolein and triricinolein. This may be attributed to the existence of double bonds in triolein and double bonds and hydroxyl group in triricinolein. The moment 2.844 for tristearin agrees with the moment 2.7 given by Stoops.⁸ As pointed out by Stoops the hydroxyl group has a moment 1.7. If this be assumed, the moment for triricinolein may be expected to be very high. Stoops, working on castor oil which contains 80% triricinolein besides small proportion of other glycerides, obtained a moment 3.7. Judging from Stoops' results alone, the present value is well within the range of the expected value. Nevertheless it may be explained that in dilute solutions when the molecules are far apart the repulsive forces in the dipole due to the intense field of the OH group may tend to separate the chains and thus make the moment smaller.

REFERENCES.

- ¹ Hartshorn and Oliver, *Proc. Roy. Soc. L.*, **123**, 661 (1929).
- ² Paranjpe and Deshpande, *Proc. Ind. Acad. Sci.*, **1**, 880 (1935).
- ³ Sudgen, *Jour. Chem. Soc.*, p. 768 (1933).
- ⁴ Allen Astin, *Phys. Rev.*, **34**, 300 (1929).
- ⁵ E. M. Colebrook, *The Wireless World*, **29**, No. 16, 276 (1932).
- ⁶ Smyth and Zahn, *Jour. Amer. Chem. Soc.*, **47**, 2501 (1925).
- ⁷ Müller and Sack, *Physikal. Zeit.*, **31**, 689 (1933).
- ⁸ W. N. Stoops, *Jour. Phys. Chem.*, **35**, 710 (1931).

THE ATTENUATION OF ULTRA-SHORT RADIO WAVES ALONG THE EARTH

BY S. R. KHASTGIR, D.Sc. (EDIN.)

AND

M. K. CHAKRAVARTY, M.Sc.

Dacca University

(Received for publication, July 15, 1935)

ABSTRACT. Relative field-strength was measured at different distances along a straight line over level earth from a portable ultra-short wave transmitter fitted with a quarter wave aerial. The transmitter was of sufficient power to enable field-strength measurements to be carried out with accuracy up to a distance of 50 m. from the transmitter. A wave length of 3.64 m. was employed for the purpose. The receiver used was a heterodyne receiver with an oscillator-detector circuit followed by I. F. power amplification. The I. F. alternating voltage developed across the telephones in the output circuit, when the transmitter was on, was measured by a sensitive valve-voltmeter constructed for the purpose. Before any attenuation measurement was made, the frequency of the beat note was adjusted whenever necessary, and brought in tune with the fixed note of a Galton whistle. All readings were taken through telescopes situated at some distance.

The attenuation measurements have been examined in the light of Norton's formula for ground attenuation of radio waves from a short dipole antenna. The values of the electrical conductivity σ and dielectric constant ϵ of the ground which give agreement with Norton's formula are :-

$$\epsilon = 7 \text{ e. s. u.}, \quad \sigma = 9.1 \times 10^{-14} \text{ e. m. u.}$$

The values for moist ground have been however larger, viz.,

$$\epsilon = 10 \text{ e. s. u.}, \quad \sigma = 1.82 \times 10^{-14} \text{ e. m. u.}$$

It is significant that these values agreed in their orders of magnitude with the values obtained by the direct laboratory method.

1. INTRODUCTION.

The problem of ground-attenuation of ultra-short waves has been engaging the growing attention of the radio-physicists. A substantial amount of work on the subject has already been done.¹ The object of this investigation has been to set up a portable ultra-short wave transmitter of suitable power and to construct a portable receiver of sufficient sensitivity so that relative

measurements within 50 m. of the transmitter can be carried out with ease and accuracy in order to obtain some reliable information on the subject of ground-attenuation of ultra-short waves. An open flat ground practically clear of obstacles has been chosen for this purpose.

2. EQUIPMENT.

The Transmitter: A low-power transmitter was constructed using a Philips T. C. 03/5 valve connected to a single tuned circuit with capacitive retro-action. The circuit diagram of the arrangement is given in figure 1. The base-board of the arrangement was fixed on the top of a wooden box containing the I. T. battery which feeds the filament. A voltage of about 200 volts was employed for the direct-current supply for the anode circuit. Suitable choke coils having self-resonance at approximately the working wave-length were used in all the D.C. supply leads to the valve electrodes.

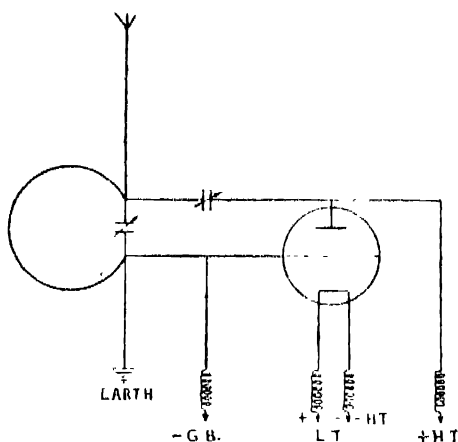


FIGURE 1.
Transmitter.

The transmitting aerial was practically a quarter wave aerial. The lower end of a straight No. 12 bare copper wire fixed in a vertical position was connected to one end of the inductance loop which was a single turn $2\frac{1}{2}$ " in diameter of $\frac{1}{8}$ " copper tube. This end was also connected to the retro active condenser. The other end of the inductance loop was connected to the earth by a metal pin struck into the ground. The short connecting wire to the earth was enclosed in an earthed metal casing. A sliding copper tube placed concentrically over the upper part of the vertical aerial was found convenient for the tuning purpose. Immediately above the inductance loop was placed a milliammeter to indicate the constancy of the aerial current.

The Receiver: The receiver constructed for the measurement of relative

field-intensity comprises a detector-oscillator unit which is identical with the transmitter just described. This stage was used in an oscillating condition for the heterodyne reception of the waves from the transmitter. After rectification the beat note of audible frequency was passed through an amplifying stage. A low-frequency choke was inserted in the anode circuit of the amplifier and a pair of telephones was connected through a large condenser ($10\mu\text{F}$) to the anode end of the low-frequency choke and the negative end of the low-tension battery feeding the filament of the amplifier. The low frequency potential difference across the telephones was then measured in arbitrary units by means of a valve voltmeter constructed for the purpose. The circuit diagram of the receiver is shown in figure 2(a). The detector oscillator valve used was a Philips T.C. 03/5 valve. The amplifying valve was a Philips B413 valve with a suitable bias voltage to the control grid. The receiving aerial was similar to the transmitting aerial.

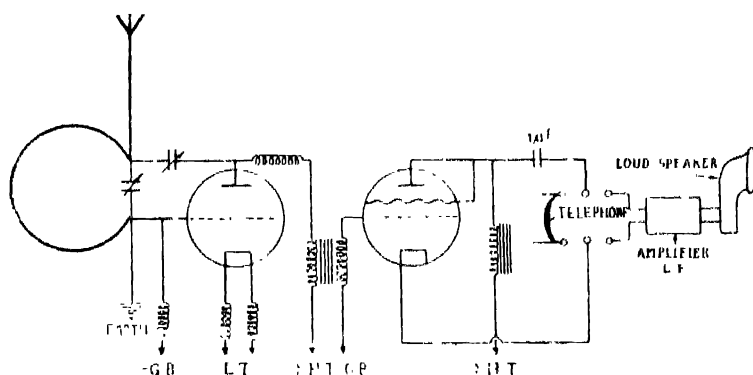


FIGURE 2(a).
Receiver.

An A. C. S. G. valve fed by direct current was employed in the valve-voltmeter. After having applied suitable voltages to the anode and the screen-grid the micro ammeter which was in the plate circuit was balanced in the manner shown in fig. 2(b). When the signal was on, a change in the deflection of the micro-ammeter was observed.

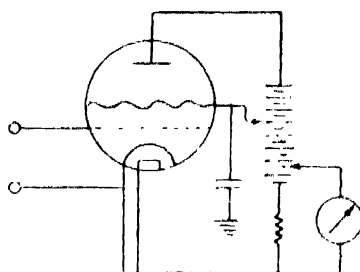


FIGURE 2(b).

The input terminals of a powerful L. F. amplifier of the conventional type was inserted when necessary in place of the telephones—the output terminals of the amplifier having been connected to a loudspeaker. Adjustment of wavelength of the oscillation in the detector-oscillator circuit was made from a distance by turning the tuning condenser with a long ebonite handle. With the transmitter on, the frequency of the continuous heterodyne whistle was thus adjusted before any valve-voltmeter measurement and brought in tune with the fixed note from a Galton whistle. Immediately after the adjustment of the tuning condenser, the amplifier was disconnected and the input terminals of the valve voltmeter connected across the telephones for the measurement of the change in micro-ammeter deflection. The change-over connections were easily made by means of a double throw over switch. In all cases, readings of the micro-ammeter deflections were taken with a telescope placed at a distance of about 5 metres from the receiver. The receiver which was enclosed in a wooden box with earthed tin linings was fixed on the top of a bigger wooden box containing the L. T. battery. The L. F. amplifier, the shielded valve voltmeter with the micro-ammeter and the H. T. dry batteries were suitably placed on the top of the big box. The complete receiving arrangement was fixed up on a wheeled carrier.

3. MEASUREMENTS OF THE RELATIVE FIELD STRENGTHS.

The procedure adopted in obtaining attenuation curves had been first to mark out the line of propagation required at definite intervals from the transmitter. The aerial current of the transmitter was adjusted to a definite value. (The observation of the aerial current was also made through a telescope situated at some distance from the transmitter.) The receiver was then taken in succession to each position and measurement of the changes in the micro-ammeter deflection made with the transmitter on and off.

Before the micro-ammeter readings were taken at each place, the beat-frequency was tested and adjusted each time to a definite value as described before.

Immediately after the measurements of micro-ammeter deflections for various distances, observation of the changes of deflections was made for different values of the aerial current at a fixed distance from the transmitter. The graph showing change of deflection against aerial current was a *straight line*. Since field-strength is proportional to aerial current, other things remaining constant, the observed changes of micro-ammeter deflections can be taken as proportional to the field-strengths. Care was taken to keep the frequency of the beat-note at a constant value during the calibration experiment. Two sets of readings are given here, one of them (called A) was taken on moist ground after a shower of rain and the other set (called B) was taken when the ground was comparatively dry.

In tables I and II are given the data for the calibration graphs and the observed changes of the micro-ammeter deflections when the ultra-short waves from the transmitter were received at different distances along a straight line up to 50 m. The calibration graphs and the attenuation curves are shown in figs. 3 and 4, respectively.

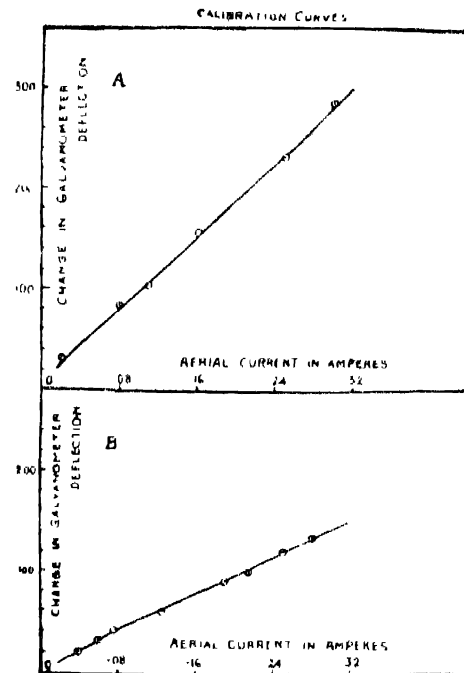


FIGURE 3.

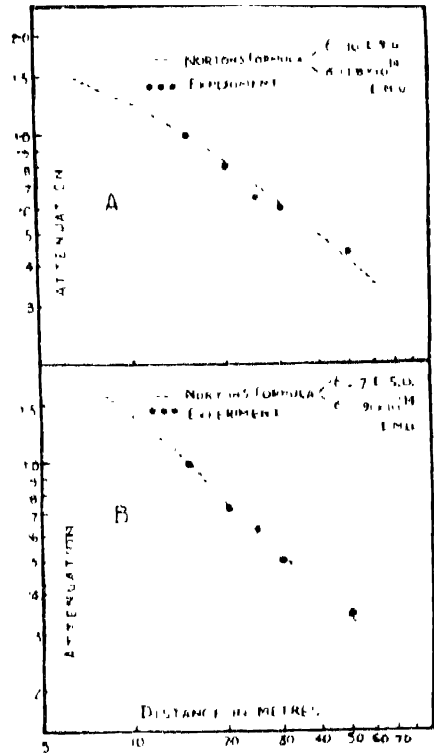


FIGURE 4.

TABLE I.

A. Wave-length = 3.64 m.

	Aerial current in amperes,	Change in micro-ammeter deflection	
Calibration Experiment at 15 m	30	287 μ A	N.B. The calibration graph is a straight line.
	25	232 "	
	16	150 "	
	11	101 "	
	08	84 "	
	02	32 "	

TABLE I (contd.).

	Distance in metres.	Change in deflection.	Relative Field-strength $\times$ distance.	
			Actual.	Reduced.
Attenuation Experiment (aerial current = 25A).	15	232	3480	1'0
	20	140	2800	'80
	25	89	2255	'65
	30	71	2130	'60
	40	70*	2800	'80*
	50	32	1600	'46

TABLE II.

B. Wave-length = 3'64 m.

	Aerial current in amperes	Change in micro ammeter deflection.	
Calibration Experiment at 15 m	'38	135 μ A	N.B. The calibration graph is a straight line
	'25	120 "	
	'15	100 "	
	'10	91 "	
	'125	60 "	
	'078	41 "	
	'06	32 "	
	'04	20 "	

	Distance in metres.	Change in deflection	Relative Field-strength $\times$ distance.	
			Actual	Reduced.
Attenuation Experiment (aerial current = 28A).	15	138	2025	1'0
	20	71	1480	'73
	25	51	1275	'63
	30	31	1020	'50
	40	40*	1600*	'70*
	50	14	700	'35

* The 40 m. site was close to a tree.

J. NORTON'S FORMULA FOR FLAT-GROUND
ATTENUATION OF RADIO WAVES

Based on the ideas of Sommerfeld,² Van der Pol and Niessen,³ Norton⁴ has recently deduced an expression for the ground attenuation factor for waves coming from a short dipole antenna. The experimental results of Feldman and Burrows have been found to agree with Norton's formula. In a recent theoretical study Norton⁵ has clearly indicated that the radiation over the plane earth consists of a space wave and a surface wave. This latter component of Norton is zero when the transmitting and receiving antennas are on the ground. Sommerfeld's 'surface wave,' however, was introduced by an error in the mathematics so that the total 'ground wave' is a space wave.

The effective height of a vertical aerial is equal to half the actual height when there is no top-loading and is equal to the actual height when the aerial has sufficient top-loading to make the current uniform throughout the vertical portion of the aerial. According to Norton the flat ground attenuation factor in the latter case is given by

$$A_1 = \left[1 + i\sqrt{\pi} p_1 e^{-p_1} \operatorname{erfc}(-i\sqrt{\pi} p_1) \right]$$

where $p_1 = p e^{ib}$

$$p = \text{"numerical distance"} = \frac{\pi}{x} \cdot \frac{1}{\lambda} \cos b = \frac{\pi}{c+1} \cdot \frac{1}{\lambda} \sin b$$

r = actual distance.

$$\tan b = \frac{c+1}{x}$$

$$x = \frac{1.8 \times 10^{18}}{f_{kc}} \cdot \sigma_{e.m.v} = 2 \frac{\sigma_{e.s.v}}{f}$$

σ = electrical conductivity of the ground.

c = dielectric constant of the ground.

f = frequency in cycles per sec.

and f_{kc} = frequency in kilocycles per sec.

5. COMPARISON OF EXPERIMENTAL RESULTS WITH
NORTON'S FORMULA

Norton has evaluated the ground-attenuation factor A_1 for different values of p and b . The calculated values have been given in a table. We made use of this table in estimating the values of A_1 for different distances from the transmitting aerial, assuming suitable values for the electrical conductivity σ and the

dielectric constant ϵ of the soil. The set A of our results agree well with Norton's formula when

$$\epsilon = 10 \text{ c. s. u. and } \frac{\sigma \epsilon \cdot 32 \pi}{f} = \frac{1}{5} \quad (f = 82 \text{ megacycles/sec.})$$

$$\text{i.e.,} \quad \sigma = 1.82 \times 10^{-11} \text{ c. m. u.,}$$

while for the set B, there is agreement with theory when

$$\epsilon = 7 \text{ c. s. u. and } \frac{\sigma \epsilon \cdot 32 \pi}{f} = \frac{1}{10},$$

$$\text{i.e.,} \quad \sigma = .91 \times 10^{-11} \text{ c. m. u.}$$

These values are in keeping with the fact that the ground was comparatively dry in the set B of our experiments. The experimental values of ground-attenuation and those calculated from Norton's formula in arbitrary units are set out for comparison in table III and figure 4. The dotted lines in figure 4 correspond to Norton's formula. The attenuation factor at a distance of 15 m. has been arbitrarily set equal to one in both sets of experiments.

TABLE III

Set A. $\epsilon = 10 \text{ c. s. u.}$ $\sigma = 1.82 \times 10^{-11} \text{ c. m. u.}$			Set B. $\epsilon = 7 \text{ c. s. u.}$ $\sigma = .91 \times 10^{-11} \text{ c. m. u.}$	
Distance in metres	Attenuation factor		Attenuation factor	
	Theory	expt.	Theory	expt.
5	1.68	—	2.87	—
10	1.24	—	1.36	—
15	1.0	1.0	1.0	1.0
20	.84	.80	.73	.73
25	.72	.65	.60	.63
30	.63	.61	.52	.50
40	.50	—	.40	—
50	.42	.46	.33	.35

It is to be mentioned here that a simple theory of attenuation of ultra-short waves from a point source (e.g., a small loop) has been worked out by J. S. McPetrie. According to McPetrie the field intensity at any point is the combined effect of the direct waves and the waves reflected from the ground at oblique incidence. Some experimental results obtained with ultra-short waves from a small loop have been published by Smith-Rose and McPetrie⁶ in support of the theory. The reflection from the ground is however implicit in the theoretical treatments of Sommerfeld, Van der Pol, Niessen and Norton.

Although some discrepancy between Norton's formula and experiment is expected at short distances due to the finite height of the transmitting aerial, it is however significant that the values of ϵ and σ computed from Norton's formula agree well in their orders of magnitude with the values obtained by the direct laboratory method.

REFERENCES

- ¹ Smith-Rose and McPetrie, *Proc. Phys. Soc.*, 43 (1931), Strutt, *Naturwiss.*, 17 (1930), C. B. Feldman, *Proc. I.R.E.*, Vol. 21, March (1933); Jones, *Proc. I.R.E.*, Vol. 21, March (1933); Trevor and Carter, *Proc. I.R.E.*, Vol. 21, March (1933); Schelleng, Burrows and Ferrell, *Proc. I.R.E.*, Vol. 21, March (1933); Englund, Crawford and Mumford, *Proc. I.R.E.*, Vol. 21, March (1933); Burrows, Decino and Hunt, *Proc. I.R.E.*, Vol. 23, Dec. (1935); Burrows, Decino and Hunt, *Elec. Engt.*, Vol. 51, January (1935); Burrows, *Proc. I.R.E.*, Vol. 25, February (1937); Burrows, *Bell System, Tech. Journal*, January (1937); Colwell and Friend, *Proc. I.R.E.*, Vol. 25, January (1937).
- ² Sommerfeld, *Ann. der Physik, Ser.*, 4, **28**, 695-736 (1909)
 " " " " " **81**, 1135-1136 (1906)
- ³ Van der Pol and Niessen, *Ann. der Physik, Ser.*, 5, **6**, 273-294 (1930)
 " " " " " **10**, 485-510 (1931).
 Niessen, *Ann. der Physik, Ser.*, 5, **16**, 810-820 (1933).
 " " " " " **18**, 803-912 (1933).
- ⁴ Norton, *Proc. I.R.E.*, **24**, 1367-1387 (1936).
- ⁵ Norton, *Phys. Rev.*, 131 (1937).
 " *Proc. I.R.E.*, Vol. 25 (1937).
- ⁶ Smith-Rose and McPetrie, *Proc., Phys. Soc.*, Vol. 41 (1932)
 " " " " " Vol. 45 (1933).

DISSOCIATION IN SULPHURIC ACID WITH TEMPERATURE

By P. KOTESWARAM,
Andhra University, Waltair.

(Received for publication, June 15, 1938.)

ABSTRACT. The effect of temperature on sulphuric acid is studied with the aid of Raman effect. As in the case of dilution, shifts are observed in the lines 533, 938 and a definite increase in intensity is noticed in the 1050 line which is attributed to the HSO_4 ion. The similarity in the changes produced by dilution and temperature is interpreted as due to the progressive dissociation of the acid even with temperature into HSO_4 and SO_4 ions. That the strong continuum usually observed in the Raman spectrum of sulphuric acid can be removed by heating it with potassium permanganate, potassium dichromate, or a trace of nitric acid or even by heating to about 200°C , is pointed out.

INTRODUCTION.

The Raman spectrum of sulphuric acid was studied by a large number of workers both in the pure state and in solutions in water. It was found that the lines of sulphuric acid in the pure state showed changes due to dilution and this was attributed to the progressive dissociation of the acid into HSO_4 and finally into SO_4 ions. Nisi,¹ Woodward,² Woodward and Horner,³ Ramakrishna Rao,⁴ and Bell and Jeppeson⁵ made a thorough study of the electrolytic dissociation of the acid by the method. To see whether there is any dissociation effected by increase of temperature, the present work was undertaken.

CONTINUOUS SPECTRUM IN SULPHURIC ACID

One feature in the Raman spectrum of sulphuric acid which was a source of great hindrance to all the workers was the strong continuous background which persisted even after repeated purifications. Woodward and Horner observed very interesting changes in the intensity of the continuous spectrum at various concentrations. Medard⁶ found that by heating the acid with a few crystals of potassium permanganate to about 150°C the continuum disappeared. The author found the same to be the case when the acid was heated with any oxidising agent, KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, or a few drops of nitric acid. The impurity giving rise to the continuous spectrum was removed thereby and the continuum

disappeared completely. The same result again was obtained by merely keeping the acid at 200°C . The picture was very clear with the Raman lines appearing conspicuously. On cooling the acid the continuum re-appeared but not with such an intensity as before heating. A filter of sodium nitrite solution shielded by Corning Noviol glass was sufficient to diminish it considerably at the lower temperature.

EXPERIMENTAL.

The acid was enclosed in vacuum in a vertical tube with a clear observation window at the top and the tube was surrounded by a heater which was kept at a constant temperature of 200°C , by adjusting the current through the coils. Light from a vertical mercury arc was condensed on to the tube by means of a cylindrical condenser filled with NaNO_2 solution shielded by Corning Noviol glass. The comparison picture at the laboratory temperature was taken after the exposure at 200°C , in order to reproduce the original spectrum at 30°C . The acid was enclosed in vacuum in the tube to prevent any contamination by moisture in the air.

RAMAN LINES IN SULPHURIC ACID

A very peculiar feature of the Raman spectrum in this acid is that all the lines are broad and diffuse. Hence it is almost impossible to locate the exact positions of their maxima by a micrometric measurement. That is the reason why the result of different authors are found to vary in their measurement of the frequencies of different lines. A microphotometric measurement will certainly be helpful in locating the exact position of the maxima of the different lines but they are subject to the usual errors of graphical interpolation. The results of different workers are given in table I; the last column gives the results of the author deduced by a microphotometric measurement. All the values of $\Delta\nu$ in are in cm^{-1} .

ASSIGNMENT OF THE DIFFERENT LINES.

The assignment of the lines in sulphuric acid was made on the basis of the results obtained by dilutions in water. Ramakrishna Rao found the 1043 cm^{-1} line increasing in intensity with dilution and hence he attributed it to the HSO_4 ion as the line is also found in acid sulphates. The 980 line which makes its appearance at higher dilutions as well as in solutions of sulphates, he identifies with the SO_4 ion; and the lines 562 , 1171 , and 1305 which could not be attributed to any radical containing the SO_4 ion but which were found to be analogous to the Raman lines of solutions of sulphur dioxide, he associates with the presence of molecules of the type $\text{SO}_2(\text{OH}_2)$. The 910 line which decreases in intensity with concentrations is due to the undissociated H_2SO_4 molecule. Woodward and

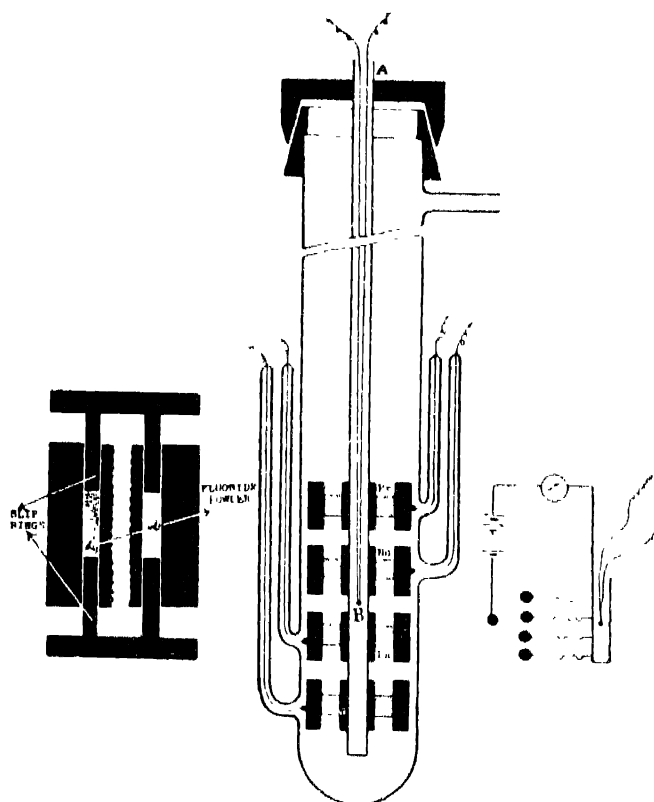


FIGURE 2.

FIGURE 3.

FIGURE 3(a).

tact with the leads to the outer electrodes connected to Ce, La, Nd, and Pr cells (Fig. 3a) and the corresponding deflections of the galvanometer were noted.

The temperature was measured by means of a copper constantan thermo-couple, a Tinsley potentiometer being used for this purpose. One junction of the thermo-couple was placed inside the copper tube ABC, somewhere near the point B.

The effect of polarisation was very appreciable at high temperatures. But below the room temperature and in vacuum it was not detectable. Below the ice-temperature the resistance increased very rapidly. Hence with the limited sensitivity of the arrangement, the observation could not be carried beyond a small range of temperature.

EXPERIMENTAL RESULTS.

The outer radius of the inner cylinder	= 1.5 cms.
„ inner „ „ outer „	= 2.0 cms.

The thickness of the Lanthanum ring	= 1.205 cms.
„ „ „ Cerium „	= 1.485 cms.
„ „ „ Praesodymium ring	= 0.606 cms.
„ „ „ Neodymium „	= 0.586 cms.

The specific resistance was calculated from the relation¹

$$\rho = \frac{2\pi RL}{\log_e(\tau_2/\tau_1)} \quad (2)$$

where

ρ = specific resistance,

R = total resistance measured,

L = thickness of rings of the compounds,

τ_1 = inner radius of the ring,

and

τ_2 = outer radius of the ring

Substituting the value of $R = \frac{E}{k\theta}$

(where k is the galvanometer constant), the specific conductivity becomes

$$\sigma = \frac{k\theta \log_e(\tau_2/\tau_1)}{2\pi EL} \quad (3)$$

The result of the experiment is tabulated below :

TABLE I.

Temperature T in °K.	$\frac{1}{T} \times 10^3$	Specific conductivity $\times 10^{13}$			
		Lanthanum.	Cerium.	Praesodymium.	Neodymium.
310	3225	4.881	69.42	32.97	20.05
308	3240	4.462	61.80	28.26	17.76
305	3278	3.068	47.26	20.78	12.61
298	3356	2.754	29.77	17.72	7.41
296	3378	2.492	29.23	14.86	7.00
281	3558	0.524	7.55	2.60	1.21
278	3597	0.439	6.37	2.35	0.99
261	3832	0.107	1.46	0.48	0.11

TABLE 1.

G.V. ⁷	N ⁸	T ⁹	B.F. ¹⁰	W. ¹¹	M. ¹²	R. ¹³	W.H. ¹⁴	B.J. ¹⁵	A.L. ¹⁶	λ
—	414	464	465	396	395	416	381	793	375	413
—	—	—	—	—	437	—	417	—	431	43 ⁸
564	564	557	567	564	560	560	555	556	561	55 ⁷
—	740	—	—	—	—	740	—	—	—	—
900	911	923	921	908	917	910	910	905	910	908
—	—	—	—	—	978	—	978	—	—	—
1045	1043	—	1045	—	—	—	—	—	1045	1000
1140	1170	1133	1128	1143	1135	1171	1121	1113	1140	1178
—	—	—	—	—	—	—	1195	—	—	—
—	1366	1326	—	1359	1373	1365	—	—	1361	1398
—	1517	—	—	—	—	—	—	—	—	—
2043	—	—	—	—	—	—	—	—	—	—
2178	—	—	—	—	—	—	—	—	—	—
2372	—	—	—	—	—	—	—	—	—	—

Horner assign the 381, 555.5, 910, 978 and 1121 lines to H_2SO_4 , 595, 595.5 and 1036 to HSO_4 and 452 and 982 to SO_4 while 417 and 1195 are common. Angus and Leckie¹⁶ and later Leckie¹⁷ do not attribute the 978 line to H_2SO_4 molecules as this line was not obtained by Bell and Jeppson who worked with the purest acid. They point out that it is due to a partial dissociation into SO_4 ions when any trace of water is present in the acid. The results of Leckie with D_2SO_4 indicate the correctness of most of these assignments but in the case of the 1048 line no isotopic shift is observed. So he feels that this line probably arises from a valency vibration involving only the oxygen atoms and thus closely related to the SO_4 frequency 685, and the frequencies at approximately 1055 in nitrates and carbonates. But the very significant change in intensity undergone by the line both with dilution and with temperature in the present work points out its origin as a HSO_4 line only. The inherent breadth of this line and its superposition on the continuous spectrum in that region might not have rendered it possible for Leckie to observe the small isotopic shift in the D_2SO_4 .

EFFECT OF TEMPERATURE ON THE RAMAN LINES.

In figure 1, are given the microphotometric curves of the Raman spectrum of the acid at two different temperatures 30°C . and 200°C . From a perusal of the curves the width of the lines is evident and at both the temperatures more than

one maximum are discernible in each line. The wave-lengths of the maxima at the two temperatures and the width of the bands as measured by graphical interpolation from the curves are given in the following table. The figures are in cm^{-1} .

TABLE II.

30°C.			200°C		
Extent	Maximum	Width.	Extent	Maximum	Width.
413-498	113,438	150	468-498	113,443-168	150
548-658	558	140	548-658	578	150
868-998	938	100	858-998	918,983	160
1098-1088	1080	60	1098-1198	1088	90
1128-1168	1178	80	1168-1388	1298	120

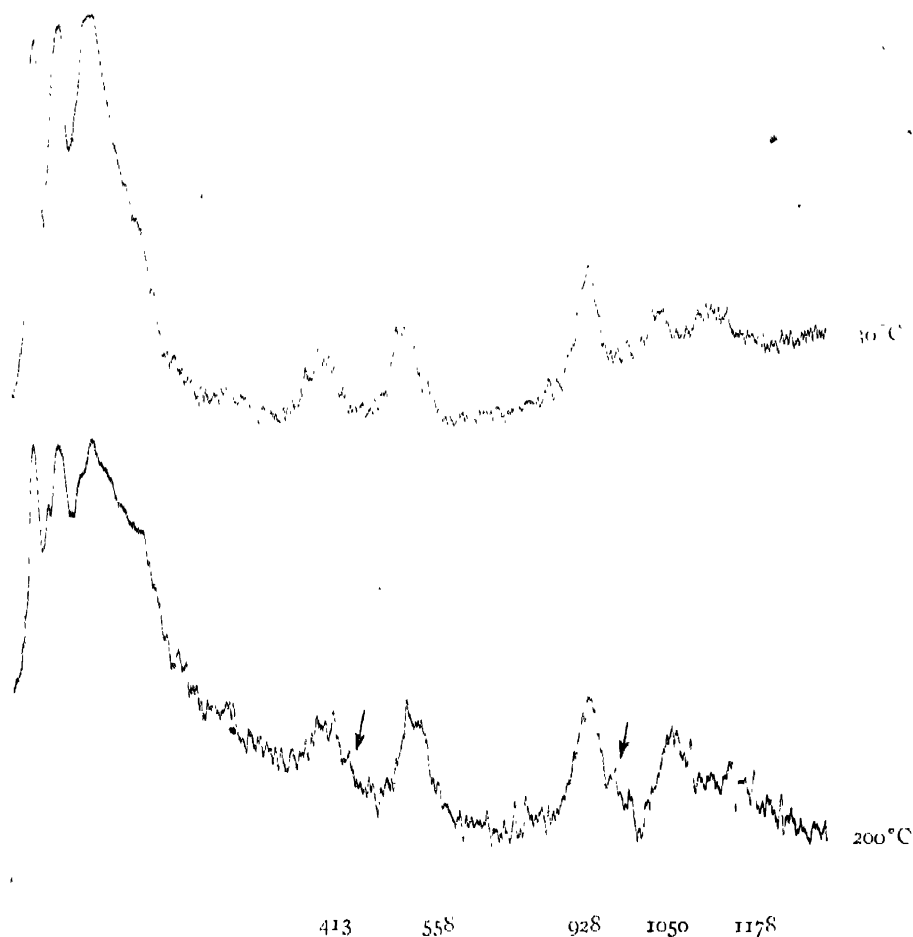


FIGURE I.

At the higher temperature the new maximum at 468 just begins to appear, the maximum at 558 shifts to 578, the single maximum at 688 shifts to 618, a new feeble maximum at 983 is just detectable, the feeble maximum at 1050 broadens up into a wide band with a maximum at 1088 with a corresponding increase in intensity, and the broad faint band with a maximum at 1178 shifts to 1123. The two bands 413 and 558 slightly decrease in their widths with increasing temperature while the other three bands increase considerably in width. More conspicuous are the intensity changes in the bands. The most prominent intensity change is observed in the 1050 band which at laboratory temperature appears as a feeble one on account of the probable presence of a slight trace of water in the acid and the subsequent formation of the HSO_4 ions. At the higher temperature the band increases in intensity and broadens itself with a single maximum at 1088. The 1178 line on the other hand decreases in intensity with increase of temperature. The 578 line is less in intensity than the 688 one at laboratory temperature, but at the higher temperature the 578 line increases in intensity such that the 578 and 923 lines are more or less of the same intensity as is clearly seen from the curves.

DISCUSSION OF THE RESULTS

The fact that each band in sulphuric acid consists of more than one maximum and that there is a shift in the maxima accompanied by an alteration in the band width with corresponding intensity changes suggests the composite nature of each band as excited by more than one type of ions. The author agrees with Woodward and Horner in the above observation in spite of Bell and Jeppson's failure to detect transitions in the frequencies of the maxima on successive dilution. By working with the acid at dilutions increasing by 5% at a time, Bell and Jeppson tried to detect particular concentrations at which they could see both the maxima appearing simultaneously. They observed a progressive shift in the maximum of each band and hence concluded that it may be due to a mere dilution shift. This observation of theirs does not disprove the assumption that the band is excited by different types of oscillators. With increasing dilutions there is a progressive formation of HSO_4 and SO_4 ions and so if one component due to one type of oscillators decreases in intensity the other due to the other type increases correspondingly and the blending of these components results in a shift in the intensity maximum.

A comparison of the results obtained by increased temperature with those obtained by dilution of the acid reveals a similarity in the effects observed. As in the case of dilution, the 558 maximum shifts to 578 and the 928 maximum shifts to the shorter wave-length side to 918. The 1050 line which is quite feeble at the laboratory temperature increases considerably in intensity and the 1120 line decreases correspondingly with a shift in its intensity maximum towards higher

frequencies. There can be no doubt about the assignment of the 1050 line to the HSO_4 ion and hence the increase in intensity of that line with temperature provides evidence for the dissociation of the acid into HSO_4 ions at higher temperatures. The similar effects noticed on other Raman lines also support the view about the dissociation of the acid at higher temperatures. The appearance of a faint 983 line and 468 maximum at 200° C (marked by arrows in the picture) indicates the formation of SO_4 ions also at the higher temperature.

As can be seen from table 2, the width of the lines undergoes significant changes with temperature. As has already been pointed out, the lines 538 and 558 slightly diminish in their width, while the other lines 928, 1050 and 1178 increase considerably. Though no exact analysis of these bands into their components can be attempted due to their inherent diffuseness, these changes in widths and shifts in the intensity maxima can be taken to indicate that each band is excited by more than one type of molecules as already discussed.

One other point requires elucidation. The lines 918, 558, 1170 and 1365 are attributed to the H_2SO_4 undissociated molecules. Of these, Ramakrishna Rao assigns the 558, 1170 and 1365 lines to a type $\text{SO}_2(\text{OH})_2$ of molecules even in the pure acid, owing to the fact that similar frequencies are found in SO_2 solution. He further refers to the fact that at increased dilutions, the lines 558, 1170 and 1365 disappear quickly as contrasted to the persistence of 918, and hence suggests that the $\text{SO}_2(\text{OH})_2$ type dissociates more rapidly than the H_2SO_4 type. There is evidence for the existence of $\text{SO}_2(\text{OH})_2$ molecules from the recent work of Venkateswaran,¹⁸ who obtained the OH band with pure sulphuric acid. In the author's temperature work, there is no contrast in the diminution of the intensities of the lines. On the other hand, the 918 line appears to diminish more than the 558 line. This indicates that increase of temperature does not probably dissociate the molecules of the type $\text{SO}_2(\text{OH})_2$ as effectively as is done in the presence of water.

The author takes great pleasure in thanking Dr. I. Ramakrishna Rao under whose guidance this work was undertaken.

REFERENCES

- ¹ Nisi, *Jap. J. Phys.*, **5**, 110 (1922).
- ² Woodward, *Phys. Z.*, **32**, 777 (1931).
- ³ Woodward and Horner, *Proc. Roy. Soc.*, **1**, **144**, 129 (1931).
- ⁴ Rao, I. R. *Ind. Jour. Phys.*, **8**, 123 (1933).
- ⁵ Bell and Jeppeson, *J. Chem. Phys.*, **2**, 711 (1934).
- ⁶ Medard, *Compt. Rend.*, **197**, 582 (1933).
- ⁷ Ganesan and Venkateswaran, *Ind. Jour. Phys.*, **4**, 196 (1929).
- ⁸ Nisi, *loc. cit.*
- ⁹ Taylor, *Trans. Farad. Soc.*, **25**, 781 (1929).
- ¹⁰ Bell and Fredricson, *Phys. Rev.*, **37**, 1562 (1931).
- ¹¹ Woodward, *loc. cit.*
- ¹² Medard, *loc. cit.*
- ¹³ Rao, *loc. cit.*
- ¹⁴ Woodward and Horner, *loc. cit.*
- ¹⁵ Bell and Jeppeson, *loc. cit.*
- ¹⁶ Angus and Leckie, *Proc. Roy. Soc.*, **149**, 327 (1935).
- ¹⁷ *Trans. Farad. Soc.*, **32**, 1700 (1936).
- ¹⁸ *Proc. Ind. Acad. Sci. A*, **7**, 13 (1938).

THERMAL COEFFICIENT OF ROCKSALT BY X-RAY REFLECTION*

By SUDHENDU BASU

AND

A. T. MAITRA, M.Sc. (PAT.),

Government Research Scholar, Science College, Patna.

(Received for publication, 17th August, 1958.)

PLATE VIII.

ABSTRACT. Thermal coefficients of expansion for rocksalt have been investigated by the X-ray reflection method from 30°C to 450°C. It has been shown that values of the coefficients will vary according as mean, true or zero coefficients are considered.

The expression for calculating the distance between the cleavage planes of rocksalt at different temperatures, up to the range investigated, has been found out to be 281400 $[1 + 0.0003162(t - 18)]$ in Å units.

The effect of temperature on the intensity of reflection from the cleavage face of rocksalt has also been studied for a few temperatures ranging up to 300°C.

1. INTRODUCTION.

Rocksalt plays an important part in the study of X-radiations. All X-ray wave-length measurements with crystals are made with respect to the grating constant of rocksalt which has been fixed at 281400 X units at 18°C. Distance between planes which are parallel to a cleavage surface of rocksalt had been calculated to be 2.814×10^{-8} cms from the knowledge of its structure. This determination involves the knowledge of the density of the crystal which varies with temperature and of the Loschmidt's number. This value of 'd' has served as the basis of all X-ray wave-length measurements with crystals. Due to large crystal imperfections in rocksalt there is not much sharpness of lines with all specimens. This characteristic of rocksalt and the difficulty of using it in all climates and the inaccuracy in the value of density have led to the discarding of this crystal in favour of calcite which possesses about the same dispersive power as rocksalt and good samples of which are easily obtained.

The grating space of calcite has been measured very accurately, on the basis of that of rocksalt, by Siegbahn¹ at 18°C. The value of grating space has to be

* Communicated by the Physical Society.

corrected when a measurement is made at any other temperature, and Siegbahn² has indicated in his book how to obtain the correct value after making allowance for thermal expansion for all ordinarily used crystals but not for rocksalt. Perhaps this has been omitted because of its restricted use and absence of reliable values of its thermal coefficient. On consulting the literature on the subject it is found that thermal coefficient of rocksalt has been determined by very few workers and from values of this constant given in table I, it will appear that there is good divergence and this coefficient has not been systematically investigated over a definite range of temperature.

TABLE I.

Temperature Range	Thermal coefficient	Worker	Method
-25°C to -15°C	10.3×10^{-6}	Lindemann ³	Optical
10°C to 60°C	10.21×10^{-6}	Fizant ⁴	
10°C to 60°C	10.91×10^{-6}	Lindemann ⁵	
28°C to 67°C	10.50×10^{-6}	Straumers and Levin ⁵	—
0°C to 110°C	33.30×10^{-6}	Saini ⁶	X-Ray Photography
110°C to 120°C	41.00×10^{-6}		
0°C to 500°C	38.33×10^{-6}	James ⁷	X-Ray Ionisation
	40.50×10^{-6}	Geiss ⁸	—

In view of the importance of rocksalt as the basis of all lattice distance measurement for X-ray purposes and because of its extensive use for greater reflective power, investigation was undertaken by the present authors to find out the value of thermal coefficients over a wide range of temperature and incidentally to determine values of ' d_{100} ' at various temperatures.

EXPERIMENT.

When a beam of X-rays of wave-length λ is incident on a crystal in a direction making a glancing angle θ with a series of atomic planes whose spacing is ' d ', the spectrum of the n th order may be taken as produced by reflection at these planes if $2d \sin \theta = n\lambda$ (1). At a higher temperature, the value of ' d ' will increase causing a displacement of the reflected line towards a smaller glancing angle θ' and the spectrum may now be represented by the relation $2d_t \sin \theta' = n\lambda$, (2), θ' being calculated from the new position of the line and n and λ being known, ' d_t ' the spacing at the temperature t becomes known.

This principle was utilised by R. W. James ⁷ in finding out the value of thermal coefficient of rocksalt between 0°C and 500°C in connection with his work on the influence of temperature on intensity of reflection of X-rays from rocksalt. As his investigation was primarily devoted to the influence of temperature on intensity, no great emphasis had been given to this part of the investigation. He followed Bragg's method of measuring angles with ionisation chambers and as such, angles measured could not be obtained with sufficient accuracy. Hence the photographic method was followed in our investigations on the lines followed by K. Becker ⁸ and others. There is no doubt as Prof. Bragg puts it, "that the method is very direct and the result cannot under ordinary precautions be affected by any change in the position of the crystal or any distortion of the apparatus."

A good specimen of rocksalt crystal was picked up from a lump bought from the local market and it was cut to proper size with extreme care in order to avoid any distortion. It was then tested for the intensity of reflection as it is our experience that all crystals do not reflect to the same extent. That the reflecting power of our crystal was very good may be seen from intense photographs b, c, d, etc., of plate VIII. The weakness of the lines of figure (a) is due to the fact that the piece of rocksalt used for temperature 450°C was different from that used in other experiments.

James ⁷ and Backhuist ¹⁰ report that even with good crystals of rocksalt the intensity of reflection becomes smaller after continued heating and that the effect is maximum with the first order reflection from the 100 face and the effect becomes less as the order of reflection increases. We had no difficulty on this score. Our specimen of rocksalt was put to a lot of preliminary heating when the heater was being designed and tested. In spite of this, as our spectrograms show, there has not been appreciable reduction in the intensity in the first order of reflection though the time of exposure was only 10 minutes with tube current 30 m-A under 50 k-V. Consequently we have taken all observations in the first order of reflection and we had this advantage over James that we could increase the intensity by increasing the time of exposure.

The crystal was raised to a high temperature by adopting the following method: A piece of mica was taken having a surface slightly greater in area than the back surface of the crystal. Nichrome wire No. 28 was used for giving a few turns over the mica piece. The heating element thus prepared was put in between two thin pieces of mica of the same size as the element. The crystal of rocksalt was laid over a thin plate of brass and the heating element, held between two pieces of mica, was placed in contact with the brass piece. The whole arrangement was then mounted on the crystal holder. The brass plate was used in order that there might be uniform distribution of heat over the whole of the crystal surface. Thick pieces of mica were put in the base of the crystal holder so that the heat might not be conducted largely to other metal parts of

the spectrometer, specially the plate holder. It was noticed that the temperature of the body of the spectrometer was only 2 or 3 degrees higher than the room temperature. Special precaution was also taken to keep the photographic plate at the room temperature. With this arrangement the temperature could be raised to 350°C. In order to increase the range of temperature further, another heating element having a rectangular opening at the middle portion, was placed in contact with the front surface of the crystal. Current was supplied from a battery of accumulators of nearly 2.1 volts and the current was adjusted with a rheostat to attain different temperatures.

The temperature was measured by a thermocouple of copper-constantan inserted inside the crystal, into an orifice bored from the top of the crystal. The hole was then completely filled up with rocksalt powder to have good contact with the surface. The e.m.f. generated in the couple was measured directly with a thermo-couple potentiometer supplied by Cambridge Instrument Company, Limited. The potentiometer readings were carefully tested and the couple was calibrated against the boiling point of water and melting points of suitable metals. From readings so obtained a temperature-e.m.f. curve was drawn.

To be sure about the uniformity and steadiness of temperature the crystal was heated for a sufficiently long time till the galvanometer deflection was found to remain steady. The exposure was only then started. As the exposure was given only for ten minutes, there was little chance of appreciable change in temperature, which was however watched by the change of galvanometer deflection. Sharpness of lines obtained at high temperature indicates that the temperature remained fairly steady during the time of exposure.

K radiations from a copper target of a Hadding-Siegbahn tube were used. The tube was worked at 30 milliamperes under a pressure of 50 kV, for all exposures excepting that for 150°C and the time of exposure was 10 mts. in all cases. As the time of exposure was short, the rating could be easily controlled. To ensure the sharpness of lines the crystal was rotated with a 1 degree cam worked by a clockwork arrangement.

As the displaced line at high temperature lies towards the decreased glancing angle, the corresponding angle was measured from the relative distance of K_{α} and K_{β} lines and the line under measurement. The relative distances were measured with the help of an accurate comparator, supplied by Adam Hilger & Co., Ltd.

3. EXPERIMENTAL RESULT

Values of ' d ', the distance between successive reflecting planes, corresponding to lines at high temperature, were measured from the well known relation $n\lambda = 2d \sin \theta$, for which the value of copper K_{α} radiation was taken from

Siegbahn's book, latest edition. For the purpose of our investigation only K_{α} radiation was considered but in a few cases the value of ' d ' was calculated both for K_{α} and K_{β} lines and it was found that values thus obtained for two different wave-lengths agreed well. Numerical values of d_{100} for various temperatures are given in table II. Observations were not made at equal intervals of temperature as it was found more convenient to measure the steady temperature reached after the heating current had been altered to a new value.

TABLE II.

Temperature °C.	Distance between atomic planes in Angstroms.	Temperature °C.	Distance between atomic planes in Angstroms.
30	2.8152	364	2.8130
130	2.8260	300	2.8170
180	2.8340	445	2.8205
250	2.8410	450	2.8050

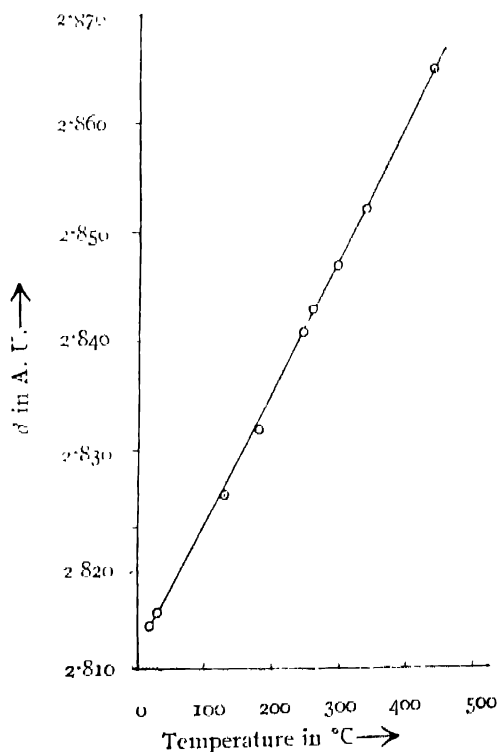


FIGURE 1.

On plotting values of ' d ' against temperature in degrees centigrade (Fig. 1) it is noticed that the change of ' d ' with temperature is quite regular and

though parabolic in nature follows nearly a straight line up to the temperature investigated by us. It will be noticed that our graph when produced backwards passes through the value of ' d_{100} ' at 18°C (2°F) as given by Siegbahn.

1. THERMAL COEFFICIENTS

The coefficient of expansion of a solid may be calculated in three ways according to the nature of the coefficient to be determined.¹¹

If l denotes the length of a specimen at temperature t and l' its length at t' , then $\alpha = \frac{l' - l}{l(t' - t)}$ measures the mean coefficient of expansion between two temperatures t' and t . Again, if l denotes the length of specimen at temperature t and l_0 its length at 0°C , the true coefficient of linear expansion at t will be $\frac{1}{l} \frac{dl}{dt}$ and the zero coefficient may be expressed as $\frac{1}{l_0} \frac{dl}{dt}$.

So far as our information goes, no worker has paid attention to this difference in the way of considering the coefficients of expansion, and it is necessary to conform to one defined method of calculating this important coefficient as the values of thermal coefficients will differ according to the expression employed in the calculation. We have attempted to study and calculate the thermal coefficients from all these different standpoints.

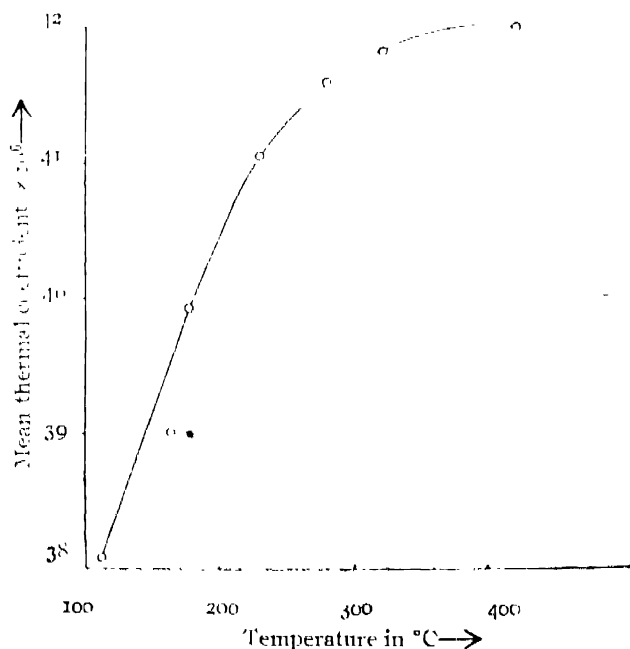


FIGURE 2.

Mean Thermal Coefficient.

The mean thermal coefficient α between $a^{\circ}\text{C}$ and $t^{\circ}\text{C}$ is a function of temperature and may be expressed by the equation $\alpha = a + bt + ct^2$ where a , b , and c are constants. In table III are given the values of this mean coefficient between 18°C and higher temperatures and the change in the values of α with the rise of temperature ($t-18$) is given in figure 2. 18°C has been regarded as the standard temperature because of the most accurate value of d_{100} at this temperature, which is known.

TABLE III.

Temperature Range.	Mean thermal coefficient $\times 10^6$.	Temperature range	Mean thermal coefficient $\times 10^6$.
18°C to 130°C	38.08	18°C to 300°C	41.68
18°C to 182°C	39.01	18°C to 315°C	41.80
18°C to 190°C	39.93	18°C to 450°C	41.07
18°C to 250°C	41.38		

Average value $= 40.53 \times 10^{-6}$

The graph in figure 2 reveals that this mean coefficient varies following a curve similar to one of sp. heat against temperature. Average value thus obtained agrees with that of many other observers. Coefficients in table III have been calculated from experimental values.

True Thermal Coefficient.

The true coefficient $\beta = \frac{1}{d} \frac{dl}{dt}$ is calculated by knowing $\frac{dl}{dt}$ from the slope of the graph between 'd' and temperature which is fairly a straight line and taking values of 'd' from the graph at definite temperatures. Values thus obtained are given in table IV.

TABLE IV.

Temperature $^{\circ}\text{C}$.	True thermal coefficient $\times 10^6$
150	41.41
200	41.32
250	41.24
300	41.15
350	41.07
400	40.99
450	40.80

Average value $= 41.15 \times 10^{-6}$

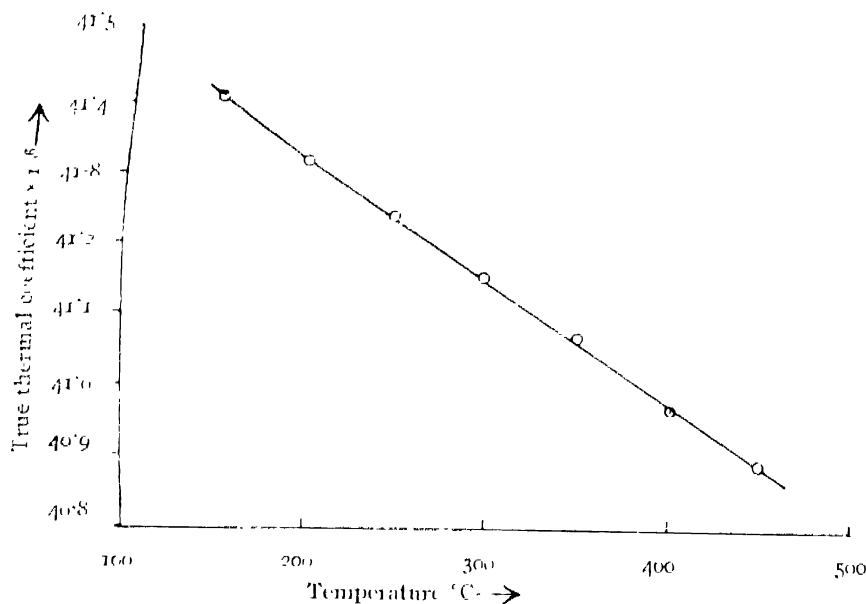


FIGURE 3.

True thermal coefficients have been plotted against temperature in figure 3 and the curve appears to confirm the expectation that this coefficient will vary inversely as temperature as the relation demands, since l varies directly as t . James has found the coefficient of expansion to be linear over the range from 0°C to 500°C , which should be nearly so when true coefficients are plotted as our graph shows.

Zero Thermal Coefficient.

Of the three thermal coefficients of expansion, the zero coefficient, $\frac{1}{l_0} \frac{dl}{dt}$ will remain constant over the range of temperature for which the curve between l and t is a straight line. Therefore, whenever the variation of length with temperature has to be represented by a simple relation of the nature $l = l_0(1 + \gamma t)$, the zero coefficient of expansion has to be used.

Now the variation of the lattice distance of crystals with temperature is represented by the relation $d_{18}\{1 + \alpha(t - 18)\}$. Therefore this coefficient should be calculated from the relation $\frac{1}{d_{18}} \frac{\delta d}{\delta t}$. We have evaluated the value

of $\frac{\delta d}{\delta t}$ from the slope of the graph in figure 2 and got the value of this coefficient for rocksalt to be 41.62×10^{-6} .

W. Geiss⁸ has stated that the lattice distance of rocksalt should be corrected by the equation $d_t = 2.81400[1 + 0.000105(t - 18)]$. As the paper of Geiss is not available to us, we cannot say how this value was arrived at. According to us, the equation for correction should be $d_t = 2.81400[1 + 0.0004162(t - 18)]$.

We have also attempted to see whether the change of temperature brings about any permanent change in the value of 'd' at the room temperature and to a certain extent whether there is any appreciable reduction in the intensity of the line as James suggests.

To test the first point, at some temperatures the photographic plate was half covered with a lead sheet. Exposure was given at the room temperature and then at a higher temperature; the lead plate was then removed and the exposure was again given at the room temperature. In some cases exposures at different temperatures were given at the same position of the plate with a portion of the plate covered with a lead sheet. Spectrograms of K line for 30°C in b, c, d, e and f of plate VII reveal that there is no displacement of lines taken twice at 30°C as it should be if there were any permanent change in the value of 'd' due to intense heating of the crystal.

In our series of exposures temperature 300°C was tried first and 130°C was tried later. But on comparing the intensity of 30°C lines as measured by a micro-photometer before the crystal was raised to 300°C and 130°C respectively, we notice that the reduction in intensity is only 20 p.c. There is no doubt that there is some diminution of intensity when the crystal is heated but we doubt whether it is of the same degree in all specimens of crystals.

5. INTENSITY OF REFLECTION AT HIGH TEMPERATURES

It is clear from simple considerations of molecular and atomic motion due to heat that the atoms in a crystal lattice vibrate about their equilibrium positions. This movement of the diffracting centres from their equilibrium positions due to the rise of temperature has the effect of lowering the intensity of the reflected X-ray beam. When a sufficiently high temperature is reached, the chance of interference would be so much lessened as to reduce the intensity to zero.

Intensity of reflection at high temperatures from the 100 surface of rocksalt has been studied by many workers and the work of W. H. Bragg, Bragg, James and Bosanquet¹¹ and James and his co-workers may be principally mentioned. All these investigations are confined to the study of the structure factor and of the validity of Debye's formula $f_T = f_0 e^{-M}$ where

f_T = atomic structure factor at absolute temperature T,

f_0 = atomic structure factor when the atom is at rest,

$$\text{and } M = \frac{3h^2}{m_a k \Theta} \left(\frac{\phi(x)}{x} + \frac{1}{4} \right) \frac{\sin^2 \theta}{\lambda^2}, \quad x \text{ being equal to } \frac{\Theta}{T},$$

or of Waller's¹² modification, $f_T = f_0 e^{-2M}$.

If R_T is the corrected integrated reflection at absolute temperature T

R_{T_1} that at any other temperature T_1 , then $R_T \propto e^{-4MT}$ and $R_{T_1} \propto e^{-4MT_1}$ according to Waller

$$\text{Therefore } \frac{R_T}{R_{T_1}} = e^{-4(M_T - M_{T_1})}$$

$$\text{or } \log \frac{R_T}{R_{T_1}} = \frac{12h^2}{m_a k \Theta} \left(\frac{\phi(x_{T_1})}{x_{T_1}} - \frac{\phi(x_T)}{x_T} \right) \frac{\sin^2 \theta}{\lambda^2}, \text{ neglecting the effect}$$

introduced by the change in the value of angle as the temperature changes

$$\text{Again we can put } \left(\frac{\lambda}{\sin \phi} \right)^2 \log \frac{R_T}{R_{T_1}} = \frac{12h^2}{m_a k \Theta} \left(\frac{\phi(x_{T_1})}{x_{T_1}} - \frac{\phi(x_T)}{x_T} \right).$$

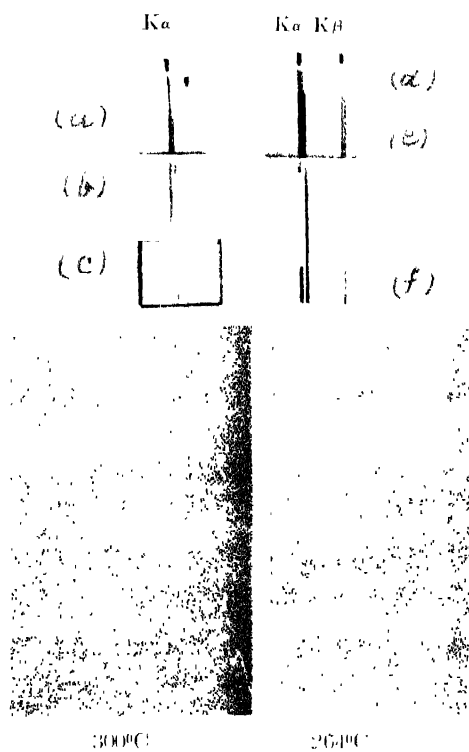
From the experimental result we can calculate the value of the left hand side of this expression. Substituting this calculated value in the expression we can calculate the value of Θ , the characteristic temperature of rocksalt.

Integrated reflection was obtained from micro-photographs of lines following the method adopted by D. K. Froman.¹³ Errors arising from nonuniformity of the emulsion or from development were none, since the lines to be compared together were close to each other. Voltage of the tube and the current passing through it were carefully controlled and as the time of exposure was short, there cannot be any error on this account.

Reproduction from two micro-photographs obtained for temperatures 26.1°C and 300°C is given in plate VIII. From it the rapid fall of intensity of reflection with the rise of temperature as also the displacement of X-ray lines both for K_α and K_β may be noticed.

In table V is given values of $\frac{R_T}{R_{30}}$ considering the reflection at 30°C to

be 1.0.



X-ray reflections from NaCl—

(a) at 182°C	(d) at 196°C
(b) „ 264°C	(e) „ 250°C
(c) „ 300°C	(f) „ 300°C

TABLE V.

Temperature °C	$\frac{R_I}{R_{30}}$
130	88
190	86.5
261	84
300	74

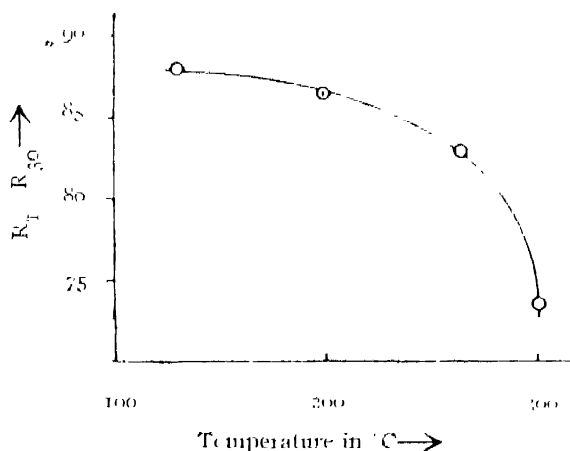


FIGURE 4.

In figure 4 is plotted $\frac{R_I}{R_{30}}$ against temperature. It is noticed that the intensity of reflection falls very rapidly as the temperature rises. Moreover it appears to fall more rapidly after 400°A indicating thereby that the effect of temperature on the intensity of reflection is not covered by either Debye's or Waller's equation—an observation recorded also by other workers.

As a test of our measurement the value of the characteristic temperature was calculated from the relation given earlier and value obtained by us agreed with that of others (282°A). Our investigation being concerned with the determination of thermal co-efficients, elaborate measurement on the effect of temperature on intensity of reflection has not been pursued, primarily due to the fact that the case of rocksalt in this respect has been adequately investigated.

In conclusion we offer our heartiest thanks to Prof. K. Prosad, B.A. (Cantab.), I.E.S., for suggesting the problem and for his interest in the work. One of us (A.T.M.) is grateful to the Government of Behar for the grant of a scholarship which has enabled him to take part in this work.

R E F E R E N C E S

- ¹ M. Siegbahn, *Phil. Mag.*, **37**, 661, **38**, 647 (1919).
- ² M. Siegbahn, *Spektroskopie Der Röntgenstrahlen*, pp. 18-48.
- ³ C. I. Lindemann, *Phys. Zeit.*, **13**, 757 (1911).
- ⁴ Eizau, *C. R.*, **64**, 314 (1867).
- ⁵ M. Straumlier and A. Levins, *Zeit. f. Physik*, **102**, 353 (1936).
- ⁶ Saint, *Helv. Phys. Acta*, **7**, 400-809.
- ⁷ E. W. James, *Phil. Mag.*, **49**, 587 (1905).
- ⁸ W. Goss, *Physica*, **4**, 115 (1911).
- ⁹ K. Becker, *Zeit. f. Physik*, **40**, 37 (1926).
- ¹⁰ I. Backhurst, *Proc. Roy. Soc. A*, **102**, 310 (1922).
- ¹¹ T. Preston, *Theory of Heat, Fourth Edition*, pp. 167-168.
- ¹² See A. H. Compton and S. K. Allison, *X-rays in Theory and Experiment*, pp. 436 and 438.
- ¹³ D. K. Froman, *Phys. Rev.*, **36**, 1330 (1930).
- ¹⁴ W. H. Bragg, *Phil. Mag.*, **27**, 881 (1911), Bragg, James and Bosanquet, *Phil. Mag.* **41**, 309 (1921).

DYNAMICS OF THE PIANOFORTE STRING AND THE HAMMER- -PART I (HARD HAMMER)

By MOHINIMOHAN GHOSH,
Burdwan Raj College (Bengal).

(Received for publication, August 31, 1958.)

ABSTRACT. Dynamics of the damped pianoforte string and the hard hammer has been worked out by the help of well-known operational method. The main idea upon which the dynamics is built up is that the string behaves like a *loaded string* so long as the hammer is in contact with it. The different cases have been worked out : (1) The hammer strikes very near the end. The expressions for the displacement and the pressure when the string is free from damping are found to be the same as those given by Kaufmann. But this method does not require to assume like Kaufmann's that the shorter segment vibrates as a rigid rod during impact which however goes *against* experimental observations. For massive hammer, expressions reduce to those that were obtained independently in a different paper. (2) The general expressions for the displacement and pressure have been also obtained, for the string struck at mid-point. Kaufmann tried this with the help of St. Venant's 'variation of integration constant.' But the method fails to include the damping of the string and also fails to give general expressions. (3) The general expressions for the same are also given for the semi infinite string struck at different points from the finite end. Das also tried this with the help of the method adopted by Kaufmann but arrived at some algebraical difficulties.

INTRODUCTION.

The dynamics of the pianoforte string and hammer was studied by a number of workers. Kaufmann¹ studied the case where the hard hammer strikes very near the end, and at mid-point. Next S. Bhargava and R. N. Ghosh² and afterwards the latter writer alone studied the case of an elastic hammer striking near the end of the string. P. Das³ studied the case of the hard and elastic hammer, striking at different points of a semi-infinite string, and pointed out a certain discrepancy in Bhargava-Ghosh's analysis. Raman and Banerjee⁴ tried to apply Rayleigh's theory of loaded string, to the case where the string is struck by a hard hammer. The expressions for the displacement of the loaded point of the string and the pressure exerted by the load, come out in the form of an infinite series. Such a

solution of course assumes that the string and the load constitute a stable system and so the string remains permanently loaded, but in the case of the struck string, it is temporarily loaded, the duration of loading being equal to the duration of impact. Recently R. N. Ghosh⁵ using the same operational method as was used by Jeffreys⁶ to solve the problem of the vibration of a string permanently loaded at the centre worked out the case where the load is attached at any point of a finite string and arrived at the expression similar to that of Raman and Banerjee. Lynger,⁷ in a paper, made an attempt to test the convergency of the infinite series obtained by Raman and Banerjee. But these workers, as is evident from their analysis, do not differentiate the dynamics of the permanently loaded string from the dynamics of the pianoforte string and the hammer. Kar⁸ pointed out that while applying the analysis for the loaded string, to obtain the solution of the vibration of the pianoforte, so long as the hammer is in contact, the idea of series should be abandoned.

None of the previous theories could explain quantitatively some of the experimental facts, such as the dependence of the duration of impact on the velocity of impact when a felt hammer impinges over a string; this was observed by Kaufmann, George,⁹ Weak¹⁰ and the author.¹¹

In a series of papers the writer alone,¹² and also conjointly with Kar,¹³ proceeding in the same line as was pointed out by one of the authors, extended the Rayleigh's theory of loaded string to the case of the pianoforte string struck by hard, elastic and felt hammer. From the general solution so obtained, it is found that Helmholtz's, Kaufmann's, Delemer's, Das's and other theories come as special cases. This is also able to explain the dependence of the duration of contact on the impinging velocity of the felt hammer.

All the above theories fail to represent the complete dynamics of the pianoforte string, *struck at any point of a finite string* and for any mass ratio of the hammer and the string.

In this paper which will appear in different parts, the author will study the complete dynamics, following operational method due to G. Boole and afterwards developed by O. Heaviside.¹⁴ These operational methods to some extent are equivalent. Only difference is, that, Boole's method leaves the integration constants to be determined separately, and Heaviside's method does not require it. The former method was adopted previously by the author to solve the dynamics of the longitudinal impact of a bar and the elastic load, and the latter method was applied by H. Jeffreys to obtain the expression for the wave propagation in strings permanently loaded at the mid-point, and in strings with continuous and concentrated loads permanently attached to them. We shall also study the criteria which mathematically differentiate the dynamics of the loaded string from that of the pianoforte string and hammer.

EXPLANATION OF THE SYMBOLS USED

l = Length of the string = $a + b$;

a = Shorter segment of the string ;

b = Longer segment of the string ;

t = Variable time ;

x = Variable, measured along the length of the string the string is fixed at $x=0$ and $x=l$;

$x_1 = x - a$;

y = Displacement at any point of the string at a given time ;

y_a = Displacement of the struck point, $x=a$;

y_1 = Displacement at any point, $x < a$,

y_2 = Displacement at any point, $x > a$;

K = Coefficient of damping ;

ρ = Linear density of the string ;

$M_1 = \rho a$ = Mass of the shorter segment of the string ;

$M_2 = \rho b$ = Mass of the longer segment of string ;

$M = \rho l$ = Mass of the string = $M_1 + M_2$,

m = Mass of the hammer ;

c = Velocity of the transverse wave motion, along the string ;

T = Tension along the string = $c^2 \rho$;

$\Theta = \frac{2l}{c} =$ Period of the free vibration of the string ;

$$\theta_1 = \frac{2a}{\Theta} = \Theta \frac{a}{l},$$

$$\theta_2 = \frac{2b}{\Theta} = \Theta \frac{b}{l},$$

$$t_n = t - n\theta_1 ;$$

v_0 = Velocity of impact ;

$$J = mv_0 ;$$

u = The compression of the hammer ;

$z = y_a + u$ = Displacement of the hammer ;

E = Elastic constant for the material of the hammer ;

P = Pressure exerted by the hammer ;

$$D = \text{Operator } \frac{d}{dt} ;$$

$$D_k = D + \frac{K}{2}.$$

The equation of motion of the damped string is

$$\frac{d^2 y}{dt^2} + K \frac{dy}{dt} = c^2 \frac{d^2 y}{dx^2}. \quad (1)$$

Now we put the usual notation D for $\frac{d}{dt}$ and consider the coefficient of damping to be small enough so that its higher power than the first may be regarded as negligible, we get from (1),

$$\frac{d^2 y}{dx^2} = \frac{D^2}{c^2} y. \quad \dots (1.1)$$

The hammer strikes at $x=a$, and if y_a be the displacement of the struck point, then, we get, proceeding in the usual manner,

$$y_1 = y_a \frac{\sinh D_k x/c}{\sinh D_k a/c}, \quad \dots (1.2)$$

$$y_2 = y_a \frac{\sinh D_k (l-x)/c}{\sinh D_k b/c}, \quad \dots (1.3)$$

The hard hammer striking the string is supposed to behave like a load attached to the string at $x=a$. Initially the string is straight, an impulse J is given to the load. The subsequent motion of the load is given by the equation

$$m \frac{d^2 y_a}{dt^2} = T \Delta \left(\frac{\partial y}{\partial x} \right)_{x=a} \quad \dots (2)$$

where $\Delta \left(\frac{\partial y}{\partial x} \right)$ denotes the alteration in the value of $\left(\frac{\partial y}{\partial x} \right)$ incurred in crossing the point $x=a$ in the positive direction.

Now substituting the value for $\Delta \left(\frac{\partial y}{\partial x} \right)_{x=a}$ as obtained from eqs. (1.2) and (1.3), in eq. (2), and imposing the boundary conditions we have

$$mD^2 y_a = -T \frac{D_k}{c} \left(\coth \frac{D_k a}{c} + \coth \frac{D_k b}{c} \right) y_a + JD, \quad \dots (2.1)$$

whence we have

$$y_a = \frac{1}{F(D)} v_0, \quad \dots (3)$$

$$\text{where } F(D) = \left[D + \frac{T}{mc} \left(1 + \frac{K}{cD} \right) \left(\coth \frac{D_k a}{c} + \coth \frac{D_k b}{c} \right) \right], \quad (4)$$

SEMI-INFINITE STRING: HAMMER STRIKES
NEAR THE END.

When b is too large compared with a , that is, the hammer strikes at a distance a of a semi-infinite string, $F(D)$ becomes, as Ll , $b \rightarrow \infty$, $\coth \frac{Dh}{c} = 1$

$$F(D) \equiv D + \frac{T}{mc} \left(1 + \frac{K}{2D} \right) \left(\coth \frac{Dka}{c} + 1 \right). \quad \dots (4.1)$$

Now $\coth \frac{Dka}{c}$ can be expanded in a series thus (*vide* Appendix, *i*)

$$\coth \frac{Dka}{c} = \frac{c}{Dka} \left\{ 1 + \frac{B_1}{2!} \left(\frac{2Dka}{c} \right)^2 - \frac{B_3}{4!} \left(\frac{2Dka}{c} \right)^4 + \dots \right\} \quad (4.2)$$

where B_1, B_3, B_5 etc. are Bernoullian numbers.

(i) When the hammer strikes very near the end, $\frac{a}{c}$ becomes very small, so that

in the expansion of $\coth \frac{Dka}{c}$, we can retain up to the second term, so eq. (4.1) becomes

$$\begin{aligned} F(D) &= D + \frac{T}{mc} \left(1 + \frac{K}{2D} \right) \left(\frac{c}{Dka} + \frac{Dka}{3c} + 1 \right) \\ &= \frac{1}{D} \left[D^2 \left(1 + \frac{\rho a}{3m} \right) + \frac{T}{mc} \left(1 + \frac{K}{3} \frac{a}{c} \right) D + \frac{T}{ma} \left(1 + \frac{K}{2} \frac{a}{c} \right) \right]. \quad \dots (5) \end{aligned}$$

From eq. (3)

$$y_a = \frac{m}{m_0} \cdot \frac{D}{(D-q)(D-p)} \cdot v_0, \text{ as } \frac{m}{m_0} \text{ is approximately equal to unity (vide}$$

eq. 6.4) ; so we have,

$$y_a = \frac{v_0}{q-p} (e^{qt} - e^{pt}), \quad \dots (6)$$

where q and p are the roots of the equation

$$D^2 + \frac{T}{m_0 c} \left(1 + \frac{Ka}{3c} \right) D + \frac{T}{m_0 a} \left(1 + \frac{Ka}{2c} \right) = 0, \quad \dots (6.1)$$

and are given by

$$\begin{aligned} q &= -\mu + i\nu \\ p &= -\mu - i\nu \end{aligned} \quad \dots (6.2)$$

where,

$$\mu = \frac{T}{2m_0c} \left(1 + \frac{Ka}{3c} \right),$$

$$v = \left[\frac{T}{m_0a} \left(1 + \frac{Ka}{2c} \right) - \frac{T^2}{4m_0^2c^2} \left(1 + \frac{2Ka}{3c} \right) \right]^{\frac{1}{2}}, \quad \dots (6.3)$$

and

$$m_0 \text{ stands for } m + \frac{\rho a}{3}. \quad \dots (6.4)$$

So we have from eqs. (6) and (6.2)

$$y_s = \frac{v_0}{v} e^{-\mu t} \sin vt \quad \dots (7)$$

When the motion of the string is free from damping we have $K=0$ in eq. (6.3) and the expression (7) becomes identically equal to what was obtained by Kaufmann, where we must read

$$\mu = \frac{T}{2m_0c} \quad \text{and} \quad v = \sqrt{\frac{T}{m_0a} - \frac{T^2}{4m_0^2c^2}}. \quad \dots (8)$$

Unlike the present method, it is not possible to include the effect of damping in the analysis adopted by Kaufmann. Further, Kaufmann assumed that the shorter segment during impact behaves like a rigid rod and used $m + \frac{\rho a}{3} (= m_0)$ for the mass of the hammer m , which according to him is the effective mass of the hammer.

A similar assumption was also made by Das, in his paper (*vide* eq. 26 of his paper) and by Bhargava-Ghosh (*vide* eq. 12 of their paper). But the author's analysis is free from such assumptions (*vide* eq. 6.4).

In this case the pressure exerted by the hammer is given by $P = m\ddot{y}_s$, which by the help of eq. (7) becomes

$$P = m \frac{v_0}{v} (v^2 + \dot{v}^2) e^{-\mu t} \sin \left(vt - \tan^{-1} \frac{3\mu v}{\mu^2 - v^2} \right) \quad \dots (9)$$

where μ and v are known from eq. (6.3) or eq. (8).

(ii) As the magnitude of $c \gg a$ we have $\frac{T}{mc} \ll \frac{T}{ma}$.

So eq. (5) becomes

$$F(D) = \frac{1}{D} \left[D^2 \left(1 + \frac{\rho a}{3m} \right) + \frac{T}{ma} \left(1 + \frac{Ka}{2c} \right) \right],$$

whence

$$y_a = \frac{D}{D^2 \left(1 + \frac{\rho a}{3m} \right) + \frac{T}{ma} \left(1 + \frac{Ka}{2c} \right)} x_0;$$

taking $\frac{m}{m_0}$ to be equal to unity, we have

$$y_a = \frac{x_0}{c\lambda} \sin \lambda c t, \quad \dots \quad (10)$$

where $\pm i\lambda c$ are the roots of the equation

$$D^2 \left(1 + \frac{\rho a}{3m} \right) + \frac{T}{ma} \left(1 + \frac{Ka}{2c} \right) = 0$$

is given by

$$\lambda c = \sqrt{\frac{T}{ma} \left(1 + \frac{\rho a}{3m} \right)^{-1}} = \sqrt{\frac{\rho}{ma} - \frac{\rho^2}{3m^2}}, \quad \dots \quad (10.1)$$

Eq. (10) is same as previously obtained in a different paper.

(iii) If a be finite, but not small enough to replace $\coth \frac{Dka}{c}$ by the first few terms of the expansion given in eq. (4.2), we have, from eqs. (3) and (4.1),

$$\begin{aligned} y_a &= \frac{1}{D + \frac{T}{mc} \left(1 + \frac{K}{2D} \right) \left(\coth \frac{Dka}{c} + 1 \right)} x_0 \\ &= \frac{1 - e^{-D_k \theta_1}}{(D + q) - D e^{-D_k \theta_1}} x_0, \end{aligned} \quad \dots \quad (11)$$

where

$$q = \left(\frac{2T}{mc} - \frac{K}{2} \right) = \frac{2\rho c}{m} \left(1 - \frac{Km}{4\rho c} \right). \quad \dots \quad (11.1)$$

On simplification,

$$\begin{aligned} y_a &= \frac{1 - e^{-D_k \theta_1}}{D + q} \left[1 - \frac{D}{D + q} e^{-D_k \theta_1} \right] x_0 \\ &= \left[\frac{1}{D + q} + \left\{ \frac{D}{(D + q)^2} - \frac{1}{D + q} \right\} e^{-D_k \theta_1} + \left\{ \frac{D^2}{(D + q)^3} - \frac{D}{(D + q)^2} \right\} e^{-2D_k \theta_1} \right. \\ &\quad \left. + + + \left\{ \frac{D^n}{(D + q)^{n+1}} - \frac{D^{n-1}}{(D + q)^n} \right\} e^{-nD_k \theta_1} \right] x_0 \\ &= f_1(t) + k[f_2(t - \theta_1) - f_1(t - \theta_1)] + k^2[f_3(t - 2\theta_1) - f_2(t - 2\theta_1)] \\ &\quad + + + k^n[f_{n+1}(t - n\theta_1) - f_n(t - n\theta_1)], \end{aligned} \quad \dots \quad (11.2)$$

$$P_1 = 2\rho v_0 c e^{-qt} \quad (1.3)$$

$$P_2 = P_1 + 2\rho v_0 c k e^{-qt_1} (1 - qt_1) \quad (1.3.1)$$

$$P_3 = P_2 + 2\rho v_0 c k^2 e^{-qt_2} \left(1 - 2qt_2 + \frac{q^2 t_2^2}{2!} \right) \quad (1.3.2)$$

$$\dots \quad \dots \quad \dots \quad \dots \quad \dots$$

$$\dots \quad \dots \quad \dots \quad \dots \quad \dots$$

$$P_{n+1} = P_n + 2\rho v_0 c k^n e^{-qt_n} \left[1 - {}^nC_1 \cdot qt_n + {}^nC_2 \cdot \frac{q^2 t_n^2}{2!} - {}^nC_3 \cdot \frac{q^3 t_n^3}{3!} + \dots + (-)^n \cdot {}^nC_n \cdot \frac{q^n t_n^n}{n!} \right] \quad (1.3.3)$$

FINITE STRING: HAMMER STRIKES AT THE MID-POINT.

In this case we put $b=a$ in eq. (4) and we get for this case,

$$F(D) = D + q \cdot \coth \frac{D_1 a}{c} = D + q \frac{1 + e^{-D_1 \theta_1}}{1 - e^{-D_1 \theta_1}} \quad (14)$$

where q is given by eq. (11.1).

The eq. (3) with the help of eq. (15) becomes

$$y_a = \left[\frac{1}{D+q} + \left\{ \frac{D-q}{(D+q)^2} - \frac{1}{D+q} \right\} e^{-D_1 \theta_1} + \left\{ \frac{(D-q)^2}{(D+q)^3} - \frac{(D-q)}{(D+q)^2} \right\} e^{-2D_1 \theta_1} + \dots + \left\{ \frac{(D-q)^n}{(D+q)^{n+1}} - \frac{(D-q)^{n-1}}{(D+q)^n} \right\} e^{-nD_1 \theta_1} \right] v_0 \quad (15)$$

(vide Appendix, vii)

$$\begin{aligned} &= f_1(t) + 2k[f_2(t_1) - f_1(t_1)] + 2k^2[2f_3(t_2) - 3f_2(t_2) + f_1(t_2)] \\ &\quad + 2k^3[4f_4(t_3) - 8f_3(t_3) + 5f_2(t_3) - f_1(t_1)] \\ &\quad + \dots + \dots \\ &\quad + 2k^n \left[2^{n-1} f_{n+1}(t_n) - 2^{n-2} \cdot \frac{n+1}{n} {}^nC_1 f_n(t_n) + 2^{n-3} \cdot \frac{n+2}{n} {}^nC_2 f_{n-1}(t_n) \right. \\ &\quad \left. - \dots - (-)^n f_1(t_n) \right] \quad (16) \end{aligned}$$

The first term is zero for negative values of times ; for positive values, i.e., during $0 < t < \theta_1$

$$y_a = f_1(t) = \frac{v_0}{q} \left(1 - e^{-qt} \right). \quad \dots \quad (16.1)$$

During $\theta_1 < t < 2\theta_1$

$$\begin{aligned} y_a &= f_1(t) + k[2f_2(t_1) - 2f_1(t_1)] \\ &= y_a(0 < t < \theta_1) - \frac{2v_0 k}{q} \left[1 - e^{-qt_1} (1 + qt_1) \right]. \quad \dots \quad (16.2) \end{aligned}$$

During $2\theta_1 < t < 3\theta_1$

$$\begin{aligned} y_a &= y_a(\theta_1 < t < 2\theta_1) + k^2[4f_3(t_2) - 6f_2(t_2) + 2f_1(t_1)] \\ &= y_a(\theta_1 < t < 2\theta_1) + \frac{2v_0 k^2}{q} [1 - e^{-qt_2} (1 + qt_2 + q^2 t_2^2)] \quad \dots \quad (16.3) \end{aligned}$$

During $3\theta_1 < t < 4\theta_1$

$$\begin{aligned} y_a &= y_a(2\theta_1 < t < 3\theta_1) + k^3[8f_4(t_3) - 16f_3(t_3) + 10f_2(t_3) - 2f_1(t_3)] \\ &= y_a(2\theta_1 < t < 3\theta_1) - \frac{2v_0 k^3}{q} \left[1 - e^{-qt_3} \left(1 + qt_3 + \frac{4}{3!} q^2 t_3^2 \right) \right] \quad (16.4) \end{aligned}$$

and so on.

The pressures exerted by the hammer at different intervals are obtained by the help of (2) and (16), and they are

$$P_1 = 2\rho v_0 c e^{-qt}, \quad \dots \quad (17.1)$$

$$P_2 = P_1 + 4\rho v_0 c k e^{-qt_1} (1 - qt_1) \quad \dots \quad (17.2)$$

$$P_3 = P_2 + 4\rho v_0 c k^2 e^{-qt_2} (1 - 3qt_2 + q^2 t_2^2) \quad \dots \quad (17.3)$$

$$P_4 = P_3 + 4\rho v_0 c k^3 e^{-qt_3} \left(1 - 5qt_3 + 4q^2 t_3^2 - \frac{4}{3!} q^3 t_3^3 \right) \quad \dots \quad (17.4)$$

$$P_5 = P_4 + 4\rho v_0 c k^4 e^{-qt_4} \left(1 - 7qt_4 + q^2 t_4^2 - \frac{20}{3!} q^3 t_4^3 + \frac{8}{4!} q^4 t_4^4 \right), \quad \dots \quad (17.5)$$

and so on.

When the hammer strikes very near the end of a long string, we find from eq. (9) that, at $t = 0$ pressure increases by sudden jump, in magnitude $2pv_0m$ which is equal to pv_0c for an undamped string. Then it continuously rises, attains a maximum value and finally falls slowly to zero at the end of the impact, the duration of which is given by $P = 0$. On the other hand, considering the rigorous expressions for pressure at different intervals as given by eqs. (13), (13.1) etc., we find that so long as the hammer is in contact, the pressure fluctuates in a definite discontinuous manner. The pressure increases by sudden jump in magnitude $2pv_0c$ at t equal to zero, whence it falls down slowly to a minimum value till at $t = \theta_1$ the pressure again rises suddenly in magnitude $2pv_0ck$. This process continues, with the sudden rise of pressures in magnitudes $2pv_0c$, $2pv_0ck$, $2pv_0ck^2$, $2pv_0ck^3$ at $t = 0, \theta_1, 3\theta_1$ respectively, till the impact terminates. The presence of k whose magnitude is less than unity lowers the successive magnitudes of the sudden rises of pressure occurring at the beginning of each interval. If the string is free from damping the pressure evidently rises by sudden jumps of constant magnitude $2pv_0c$. The nature of the pressure

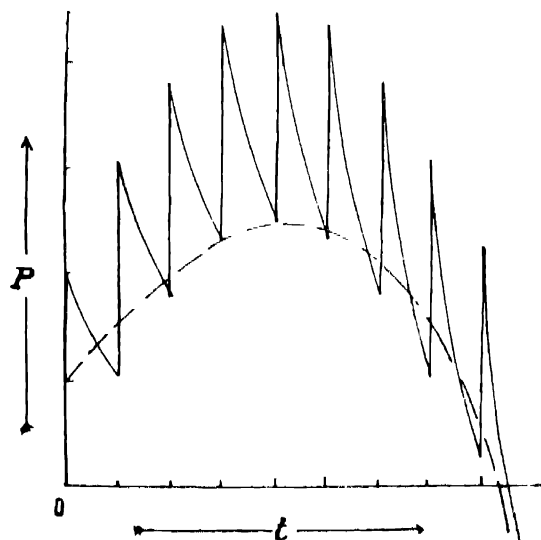


FIGURE 1.

fluctuation, as following from the theory, is shown graphically in Figure 1. The continuous curve from eq. (9) is shown dotted in the figure. The discontinuous curve represents the pressure as given by eqs. (13), (13.1) etc. for undamped string. It is evident from the graph that the continuous curve represents approximately the mean values of the discontinuous curve; and it will be the actual mean curve when the number of discontinuities is very large, which is the case when the length of shorter segment is very small.

The pressure exerted by the hammer when it strikes at the mid-point of a finite string also fluctuates discontinuously, as is evident from eqs. (18), (18.1) etc. But the sudden rise of pressure at $t = 0$ is $2pv_0c$, but subsequently at $t = \theta, 2\theta, \dots$, the rises are constant and of magnitude $4pv_0c$ in the case of undamped string, till the pressure terminates.

My best thanks are due to Prof. K. C. Kar, D.Sc., of Presidency College, Calcutta, who has taken a lively interest in this work.

A P P E N D I X.

$$(i) \quad \coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}} = \frac{1 + e^{-2x}}{1 - e^{-2x}} \quad \dots (1)$$

$$= \frac{1}{x} \left\{ 1 + B_1 \frac{(2x)^2}{2!} - B_3 \frac{(2x)^4}{4!} + B_5 \frac{(2x)^6}{6!} - + \dots \right\}, \quad (2)$$

where $B_1 = \frac{1}{6}$, $B_3 = \frac{1}{30}$, $B_5 = \frac{1}{42}$, $B_7 = \frac{1}{30}$, $B_9 = \frac{5}{66}$ and they are known as Bernoullian numbers.

$$(ii) \quad \text{Lt. } x \rightarrow 0 \quad \coth x \rightarrow \frac{1}{x} \left(1 + \frac{x^2}{3} - \frac{x^4}{45} \right) \rightarrow O(\infty) \quad \dots (3)$$

$$\text{Lt } x \rightarrow \infty \quad \coth x \rightarrow 1, \text{ from eq. (1)} \quad \dots (4)$$

$$\begin{aligned} (iii) \quad \frac{D}{(D+q)^n} \cdot v_0 &= D^{-(n-1)} \cdot (1 + qD^{-1}) \cdot v_0 \\ &= \left[D^{-(n-1)} - nqD^{-n} + \frac{n(n+1)}{2!} q^2 D^{-(n+1)} \right. \\ &\quad \left. - \frac{n(n+1)(n+2)}{3!} q^3 D^{-(n+2)} + \dots \right] v_0 \\ &= v_0 \left[\frac{t^{n-1}}{(n-1)!} - nq \frac{t^n}{n!} + n(n+1) q^2 \frac{t^{n+1}}{(n+1)!} - + \dots \right] \\ &= v_0 \frac{t^{n-1}}{(n-1)!} e^{-qt} \quad \dots (5) \end{aligned}$$

$$\begin{aligned} (iv) \quad \frac{D^n}{(D+q)^{n+1}} \cdot v_0 &= D^{n-1} \cdot \frac{D}{(D+q)^{n+1}} \cdot v_0 \\ &= v_0 D^{n-1} \frac{t^n}{n!} e^{-qt} \end{aligned}$$

$$\begin{aligned}
 &= v_0 e^{-qt} (D - q)^{n+1} \frac{t^n}{n!} \\
 &= v_0 e^{-qt} \left[D^{n+1} - {}^{n+1}C_1 \cdot D^{n+2} q + {}^{n+2}C_2 \cdot D^{n+3} q^2 + \dots \right. \\
 &\quad \left. + (-)^{n+1} q^{n+1} \right] \frac{t^n}{n!} \\
 &= \frac{v_0}{q} e^{-qt} \left[qt - {}^{n+1}C_1 \frac{q^2 t^2}{2!} + {}^{n+1}C_2 \frac{q^3 t^3}{3!} \right. \\
 &\quad \left. - \dots + (-)^{n+1} \frac{q^n t^n}{n!} \right] \\
 &= f_{n+1}(t); \quad \dots (6)
 \end{aligned}$$

whence we have from eq. (5) or (6)

$$\frac{1}{D+q} v_0 = \left[1 - \frac{D}{D+q} \right] \frac{v_0}{q} = \frac{v_0}{q} (1 - e^{-qt}) = f_1(t) \quad \dots (7)$$

and $\frac{D}{(D+q)^2} v_0 = f_2(t) = v_0 \frac{e^{-qt}}{q} \cdot qt \quad \dots (8)$

$$\frac{D^2}{(D+q)^3} v_0 = f_3(t) = v_0 \frac{e^{-qt}}{q} \left(qt - \frac{q^2 t^2}{2!} \right); \quad \dots (9)$$

$$\frac{D^3}{(D+q)^4} v_0 = f_4(t) = v_0 \frac{e^{-qt}}{q} \left(qt - 2 \frac{q^2 t^2}{2!} + \frac{q^3 t^3}{3!} \right); \quad \dots (10)$$

and so on.

$$\begin{aligned}
 (v) \quad e^{-\lambda D} \cdot f_n(t) &= \left(1 - \lambda D + \frac{\lambda^2 D^2}{2!} - \frac{\lambda^3 D^3}{3!} + \dots \right) f_n(t) \\
 &= \left\{ f_n(t) - \lambda f'_n(t) + \frac{\lambda^2}{2!} f''_n(t) - \frac{\lambda^3}{3!} f'''_n(t) + \dots \right\} \\
 &= f_n(t - \lambda) \quad \dots (11)
 \end{aligned}$$

$$\begin{aligned}
 (vi) \quad \frac{(D-q)^n}{(D+q)^{n+1}} \cdot v_0 &= \frac{(2D-D_1)^n}{D_1^{n+1}} \cdot v_0, \text{ where } D_1 \text{ stands for } (D+q) \\
 &= [2^n D^n - {}^nC_1 2^{n-1} \cdot D^{n-1} \cdot D_1 + {}^nC_2 2^{n-2} \cdot D^{n-2} D_1^2 \\
 &\quad - \dots + (-)^n D_1^n] D_1^{-(n+1)} \cdot v_0 \\
 &= \left[2^n \frac{D^n}{(D+q)^{n+1}} - {}^nC_1 2^{n-1} \frac{D^{n-1}}{(D+q)^n} + {}^nC_2 2^{n-2} \frac{D^{n-2}}{(D+q)^{n-1}} \right.
 \end{aligned}$$

$$\begin{aligned}
& - + \dots + (-)^n \frac{1}{D+q}] v_n \\
& = [2^n f_{n+1}(t) - {}^nC_{1,2}{}^{n+1} f_n(t) + {}^nC_{2,2}{}^{n-2} f_{n-1}(t) \\
& \quad - + \dots + (-)^n f_1(t)]. \quad \dots (12)
\end{aligned}$$

$$(vii) \left[\frac{(D-q)^n}{(D+q)^{n+1}} - \frac{(D-q)^{n-1}}{(D+q)^n} \right] v_n, \text{ (from eq. (12))}$$

$$\begin{aligned}
& = 2^n f_{n+1}(t) - 2^{n-1} \cdot \frac{n+1}{n} \cdot {}^nC_1 f_n(t) + 2^{n-2} \cdot \frac{n+2}{n} {}^nC_2 f_{n-1}(t) \\
& \quad - 2^{n-3} \cdot \frac{n+3}{n} {}^nC_3 f_{n-2}(t) + \dots + (-)^n 2 f_1(t), \quad \dots (13)
\end{aligned}$$

whence,

$$\left[\frac{D-q}{(D+q)^2} - \frac{1}{D+q} \right] v_n = 2f_2(t) - 2f_1(t) \quad \text{from eq. (12) and (7);} \quad \dots (14)$$

$$\left[\frac{(D-q)^2}{(D+q)^3} - \frac{D-q}{(D+q)^2} \right] v_n = 4f_3(t) - 6f_2(t) + 2f_1(t) \quad \text{from eq. (13);} \quad \dots (15)$$

$$\left[\frac{(D-q)^3}{(D+q)^4} - \frac{(D-q)^2}{(D+q)^3} \right] v_n = 8f_4(t) - 10f_3(t) + 10f_2(t) - 2f_1(t); \quad \dots (16)$$

and so on.

REFERENCES.

- 1 Kautmann—*Ann. d. Phys. u. Chem.*, **54**, 375 (1895).
- 2 Bhargava, S. and Ghosh, R. N.—*Phil. Mag.*, **47**, 1141 (1924); **49**, 121 (1925).
- 3 Das, P.—*Proc. Ind. Assoc.*, **7**, 13, (1921); **10**, 207 (1926), **10**, 75 (1926); *Ind. J. Phys.*, **1**, 437 (1927); *Phys. Soc. Proc.*, **40**, 29 (1927).
- 4 Raman, C. V. and Banerjee, B.—*Proc. Roy. Soc.*, **97**, 99 (1920).
- 5 Ghosh, R. N.—*Proc. Acad. Sci., (U.P.) Ind.*, **5**, 15 (1935).
- 6 Jeffreys, H.—*Operational methods in Mathematical Physics*, Cambridge University (1931), p. 57, Art. 4.4, *Proc. Camb. Phil. Soc.*, **23**, 768 (1927).
- 7 Ivenger, K. V.—*Proc. Ind. Acad. Sci.*, **1**, 60 (1934).
- 8 Kai, K. C.—*Ind. Phys. Math. Jour.*, **3**, 103, (1932); also *Phil. Mag.*, **6**, 276 (1925).
- 9 George, W. H.—*Phil. Mag.*, **48**, 34 (1924).
- 10 Weak, C. K.—*Amer. Jour. Sci.*, **32**, 366 (1895).
- 11 Ghosh, M.—*Ind. J. Phys.*, **7**, 356 (1932).
- 12 Ghosh, M.—*Phil. Mag.*, **17**, 521 (1921); *Ind. Phys. Math. Jour.*, **3**, 15 (1932); Kar and Ghosh—*Phil. Mag.*, **9**, 306, 321 (1930), **12**, 276 (1931); *Zeit. f. Phys.*, **61**, 525 (1930), *Zeit. f. Angew. Math. Mech.*, **11**, 361 (1931).
- 13 Ghosh, M.—*Ind. Phys. Math. Jour.*, **3**, 73 (1932); *Zeit. f. Angew. Math. Mec.*, **14**, 71 (1934), *Bull. Cal. Math. Soc.*, **27**, 1 (1935), Ghosh and Dhar—*Ibid.*, **27**, 171 (1935).
- 14 Heaviside, O.—*Proc. Roy. Soc. A.*, **52**, 504 (1893) See also Ref. (6).

ON THE HYPER-FINE STRUCTURE AND ANALYSIS OF SOME COMPLEX LINES IN THE FIRST SPARK SPECTRUM OF ARSENIC IN THE ULTRA- VIOLET REGION

BY DR. S. K. MUKERJI, M.Sc., Ph.D. (LONDON),

Professor of Physics, Agra College, Agra

(Received for publication, August 30, 1938)

Plate IX

ABSTRACT All the important lines in the region $\lambda\lambda 3200-2400$ of the first spark spectrum of arsenic emitted by a water-cooled hollow cathode discharge have been investigated, with a quartz Lummer plate, for hyper-fine structure. An attempt has been made to analyse the incompletely resolved and complex lines, assuming the nuclear spin of arsenic to be $3/2$ as previously determined. An estimate has also been made of the values of the fine-structure intervals and the term interval factors of the lines investigated. One of the unclassified lines has shown an inverted structure. Fine structure perturbation effect is suspected in one of the partially classified lines.

INTRODUCTION

The hyper-fine structure of the first spark spectrum of arsenic has been investigated by S. Tolansky¹ and also by A. S. Rao² in the visible region. But no investigation has so far been made on the hyper-fine structure of any of the lines of the first spark spectrum of arsenic in the ultra-violet region. The present paper deals with the fine structures of some of the complex and incompletely resolved AsII lines in the ultra-violet region and an attempt has been made to analyse such lines. In a recent paper³ the author has already shown, as previously proposed by S. Tolansky, (*loc. cit.*), that the nuclear spin of arsenic is $3/2$. In this investigation the nuclear spin of arsenic has been assumed to be $3/2$, and the gross-structure multiplet analysis of AsII lines and the line classifications as made by A. S. Rao⁴ have been employed. Amongst the other lines analysed or an attempt has been made to analyse are those involving terms designated by Rao as—A, B, D, E, F. Also it has been found possible to check the fine structures of a number of terms in as much as they are involved in two or more line transitions the structures of which have been determined. The usual constant frequency difference method of analysis is employed in the case of well resolved lines showing simple structures whilst in the case of complex and incompletely resolved lines as one has been analysed

here, the Fisher-Goudsmit⁵ graphical method of analysis has been employed. This method, as will be seen later, has been found extremely useful in the analysis of complex structures.

EXPERIMENTAL

The apparatus used is similar to that described by the author in his previous paper (*loc. cit.*). The spark spectrum was excited in a water-cooled hollow cathode containing arsenic as described in that paper and pure helium was circulated continuously through the tube at a pressure of about one millimetre. The hollow cathode being at a high current density with a vapour such as arsenic is extremely unstable and hence a high ballast resistance was used to maintain constancy of current. This necessitated the use of high voltage at the source and a current of 300-500 milli-amperes. The arsenic was heated in vacuum, as explained in the previous investigation, and a brilliant spectrum of arsenic was then obtained. Ilford Monarch plates speed 525, were used for this part of the spectrum and the exposure times varied from four to seven hours. The temperature and pressure variations were negligible but a few lines in spite of being fairly strong have only shown unresolved broad structures. As the analysis will show later, such lines are mainly complex lines with fairly high J values. The terms split up into a number of fine structure levels giving a large number of line structure components which cannot be resolved by the Lummer plate. This difficulty is still greater when the widths of both the upper and lower terms are of the same order. Moreover, on the shorter wave-length side in the ultra-violet region the Doppler width of the lines, measured in frequency units, increases with the frequency. The Stark broadening and line width due to collision phenomena also at the same time increase in the same manner. Therefore, the practical separating power, as measured by the smallest frequency distance between two lines that can be resolved, steadily increases with frequency. Hence, it will be appreciated that in some cases it has only been possible to determine the total width of a pattern, as with a complex group of fine structure components in the ultra-violet region no single component can be resolved. In such cases, therefore, it is only possible to make an estimate of the intervals, further checks being of course obtained from the measurements of other lines which show good resolution and which involve common terms.

Further details of the apparatus used and the experimental arrangements made will be found in a previous paper.⁶

ANALYSIS

There are no isotopic complications in the structures of arsenic lines but when the structure is complex and the components are incompletely resolved as in the case of a line analysed here it is found that the Fisher-Goudsmit method

of analysis is particularly valuable. A brief description of this method has already been published.⁷

The details of the analysis of the individual lines will now be given and the determination of the structures of the terms will also be considered. The lines have been examined in the order best suited for analysis and the results obtained have also, where possible, been checked by examining the structures of more than one line involving common terms. The Fisher-Goudsmit method is employed only in the case of incompletely resolved and complex lines as explained before.

The analysis of the lines is given below.

$$\lambda 2890.21 (4d^3F_3 - D), \lambda 2884.51 (4d^3F_3 - E), \lambda 2830.45 (4d^3F_3 - F).$$

These three lines all show very similar structures and therefore they will be dealt with together. They are sharp though weak doublets degrading in intensity to the violet. They are also all of nearly the same widths. It is obvious, therefore, that the structures in each must approximate very closely to the structure of the common $4d^3F_3$ term. The term line structure multiplicity is $2I+1$ or $2J+1$, according to which has the smaller value. The term $4d^3F_3$ should then be a quartet. (Here $I=3/2$ and $J=3$. Therefore $2I+1=4$.) The terms D, E and F evidently have no contribution in the structure of these lines. Therefore they are all very narrow. The slight variations in the values of the doublet widths of these lines are then due to the slight differences in the structures of these terms. The line, $\lambda 3116.03 (4d^3F_3 - B)$ the analysis of which follows next, is of the same type. It has got the $4d^3F_3$ term common. It exhibits four components instead of two, as theoretically expected though on a smaller scale. This is strongly suggestive of the fact that the above three lines are actually quartets but owing to the extreme weakness of these lines the last two components being still more feeble are not observed on the plates. If this conclusion be correct it is possible then to determine the mean approximate value of the interval factor of the term $4d^3F_3$, of course, on the assumption that the interval rule holds in this term. It is remarkable that this term which has no penetrating electron should show such a large interval factor.

$$\lambda 3116.03 (4d^3F_3 - B)$$

This line deserves particular attention. It consists of four sharp narrow components well separated from one another and degraded to the violet. The intervals are 190, 150 and 205. It has shown a coarse structure, the total width being slightly smaller than, but of the same order of magnitude as, that of the three lines discussed above. It is therefore strongly suggestive that the B term is small but it may not be negligible. Of particular interest is the fact that although the interval rule holds between 190 and 150, there is a complete break-down and a very large deviation from the interval rule between 150 and 205. This seems to indicate that a fine structure perturbation effect has taken place in this line which is not to be expected in the above three lines which have all

shown almost the same structure. Usually fine structure perturbation is supposed to take place between two terms of different J values so that the fine structure levels with the same F values suffer an apparent repulsion⁸ and this thereby distorts the levels. This breakdown of the interval rule may be due to this cause. Further explanation of this is given later.

$$\lambda 3058.08 (4d^3F_2 - A).$$

This line also shows four components with a fairly wide structure. The first two components are well separated and sharp but the separation between the last two components is not very good. They degrade in intensity and intervals to the violet. Analysis of the line $\lambda 3053.46$ which follows next shows that the term A should have negligible structure. If that be so, the line structure should be the term structure of the term $4d^3F_2$. The observed intervals are 243, 183, and 157. If the Lande interval rule holds exactly, the intervals should be 243, 175 and 105. The error in the second interval is ± 8 units and that in the last it is much more; unless this be a case of perturbation, it is probably due to the fact that the last two components were not well resolved. Hence, as the first two components reasonably obey the interval rule it is fairly safe to assume that in the $4d^3F_2$ term the interval rule is valid, and that the structure of this term is represented by these values. If that be so, the interval factor of this term should be about 72. That this value is correct is further verified by the analysis of the line $\lambda 3053.46$ which follows next. The predicted and observed patterns are shown in figure 1(a).

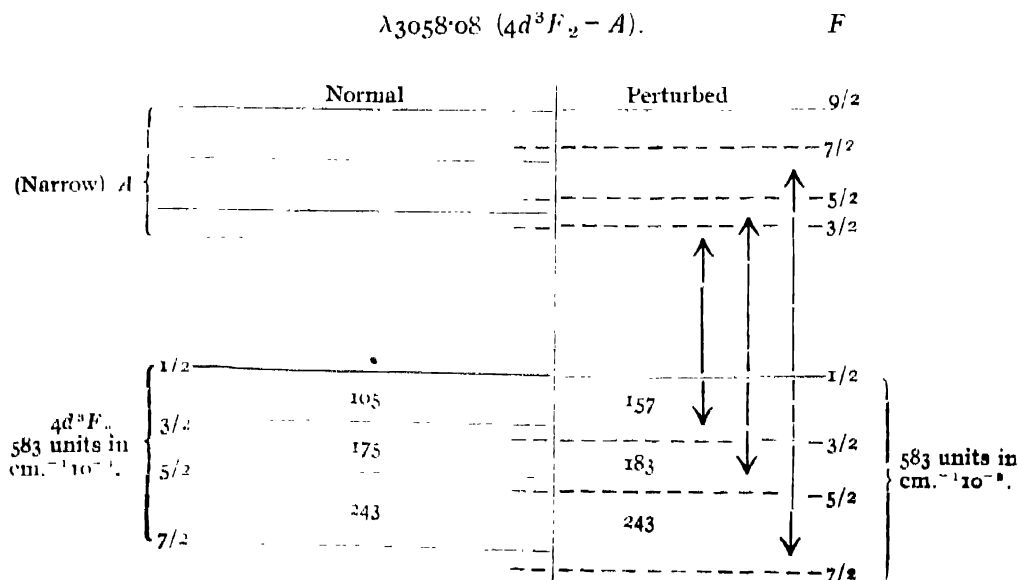


FIGURE 1(a)

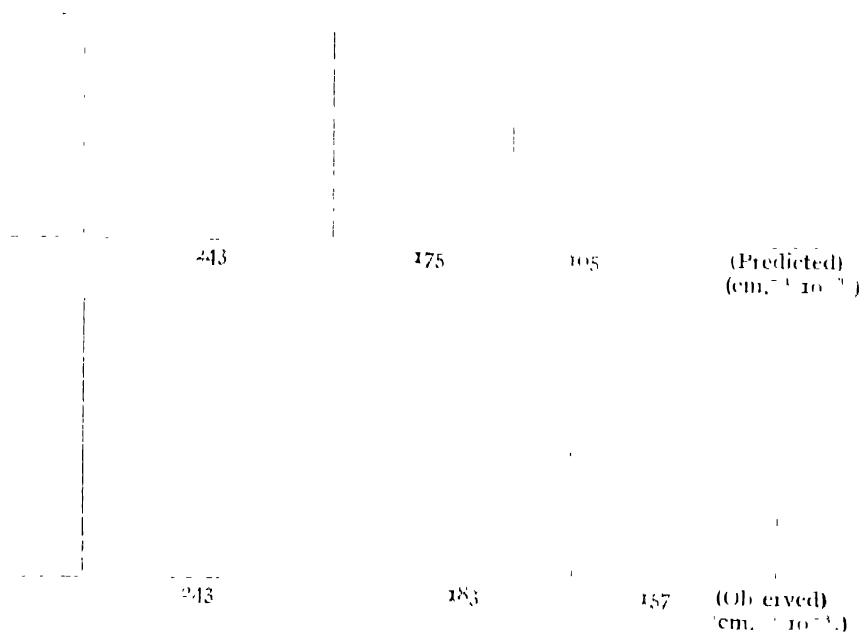


Fig. 1(b)

If the distortion of the levels is real, it would indicate that a fine-structure perturbation effect has set in. This is explained by a diagram shown in Fig. 1(a).

Fine structure perturbation is supposed to take place between two terms with different J values. Hence, it is assumed that since the J value of the lower term is 2, the J value of the unknown upper term is 3. Thick lines at the left of the figure show the unperturbed or the normal levels obeying Landé's interval rule and the dotted lines at the right the perturbed levels. Repulsion is supposed to take place between fine structure levels with the same F value. The levels with F equal to $3/2$, $5/2$, $7/2$, find their counterparts in both the upper and lower structures and hence repulsion only takes place between these levels. This is shown by thick vertical arrows in the figure. It will be seen that the lower $F=1/2$ level is not perturbed. But since the value of the displacement is such that the interval rule still holds only in the displaced terms, the interval rule breaks down in the $4d^3F_2$ term. Therefore it will be seen that the distance between the fine structure levels $F=1/2$ and $F=3/2$ becomes much wider than what is allowed by the interval rules. This may, therefore, be the possible explanation of the anomaly observed in the structure of this line.

$$\lambda_{3053.46} (4d^3F_2^o - 4f^3F_3).$$

This is a complex line showing six components poorly resolved and very close together. This is a line suitable for analysis by the Fisher and Goudsmit

method. For this purpose the Fisher-Goudsmit diagram is to be drawn first. This is shown in figure 2. This diagram, as explained before, is built up by giving both the upper and lower terms the same interval factor, that is, the ratio of the upper and lower interval factors is made equal to $\mu = \pm 1$ and the resulting line structures are then plotted as points along the straight line AB. This line therefore represents the structure observed when the ratio of the upper to the lower interval factor is $+1$. The upper term is then completely inverted and the line

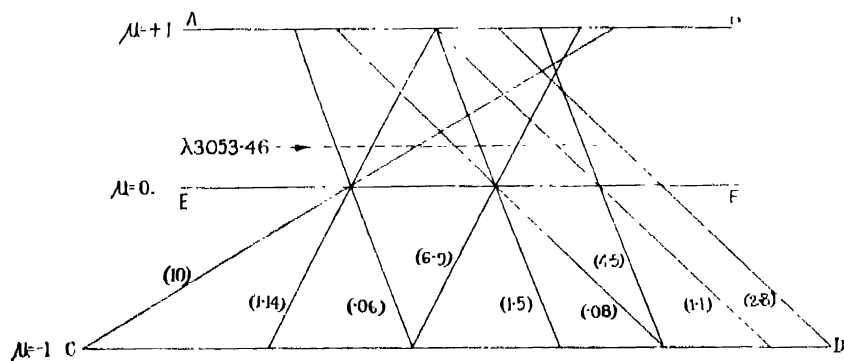


FIGURE 2

$$\lambda_{3053.46} (4d^3F_2 - 4f^3F_3).$$

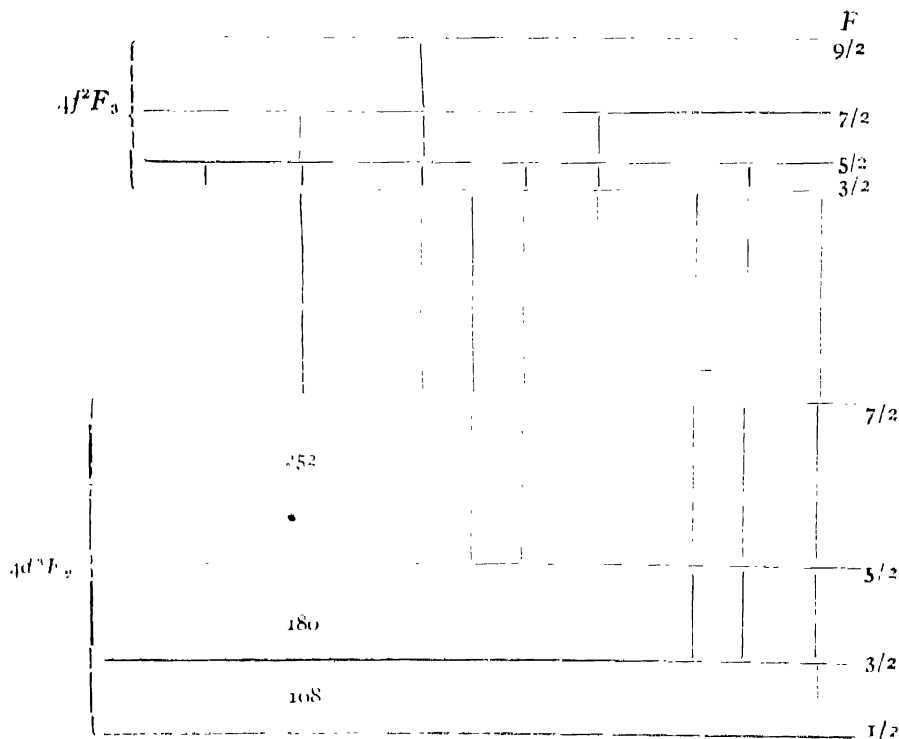


FIGURE 3

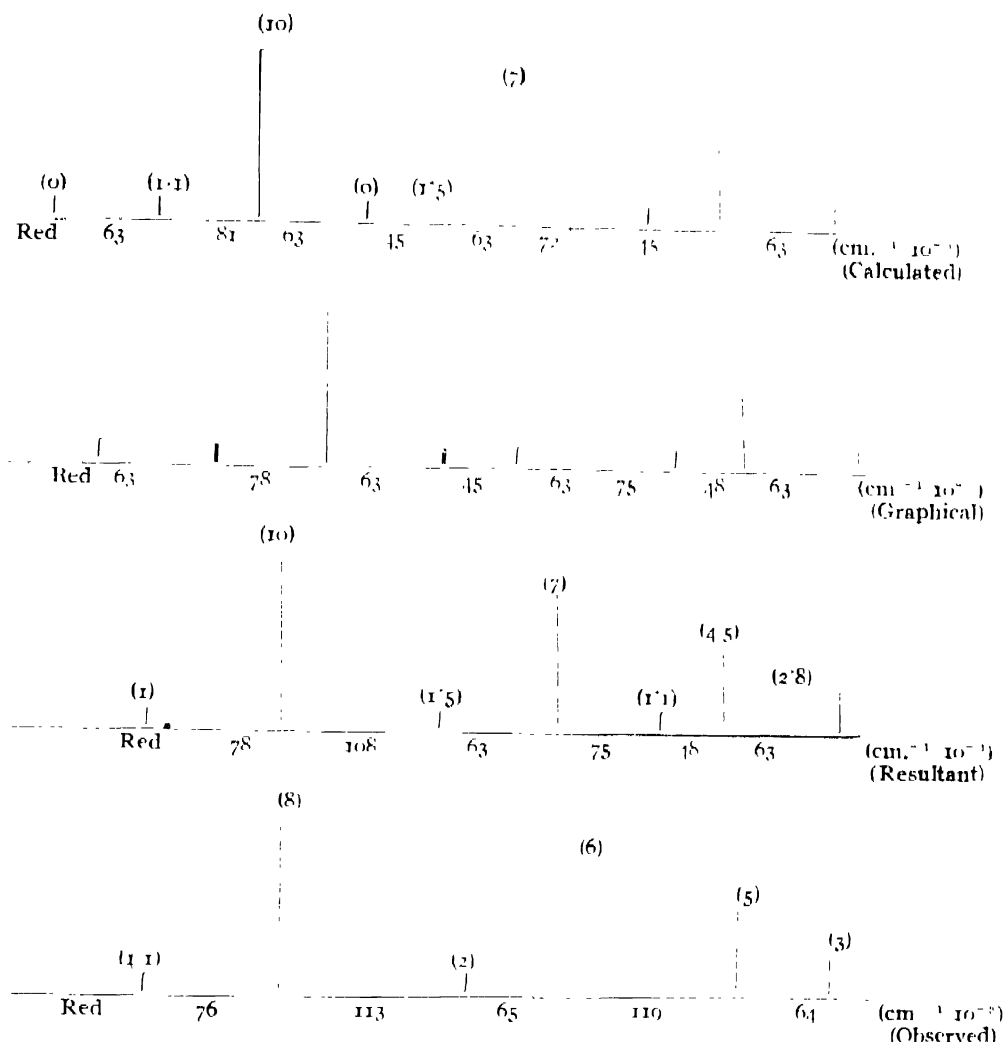


FIGURE 3 (contd.)

CD drawn parallel to AB then represents the line complex formed by all the possible transitions, the interval factor being kept still the same. This line then shows the structure when the ratio of the upper to the lower interval factor is $\mu = -1$. The corresponding transitions in AB and CD involving identical F values are then joined by straight lines, their breadths being made roughly proportional to the intensities of the transitions or as shown in the diagram, the intensities are directly obtained and noted down from the Relative Intensity Tables of White and Eliason (*loc. cit.*). The observed line is then made to fit this graph along some particular horizontal position and this position gives the values of both the upper and lower interval factors. In this particular case it is found that this line fits very nicely at a ratio of the lower to the upper interval factor of 1 to 1, that

is, 72 to 18. Both methods of analysis have been used and it is found that the agreement is remarkably good with 72 and 18 as the interval factors of these two terms. But 72 has been obtained as the interval factor of the term $4d^3F_2$ from the analysis of the line $\lambda 3058\cdot08$ on the assumption that the structure of A is very small. Hence this analysis supports the validity of this assumption. The predicted, graphical, resultant and observed patterns are shown in figure 3, and the Fisher-Goudsmit diagram, as described before, is shown in figure 2. It will be seen that the agreement is quite good although the very weak component $3/2-3/2$ is missing

$$\lambda 4431\cdot73 \quad (4d^3D_1 - 4f^3F_2).$$

This line although in the visible region has also been examined as it contains the term $4f^3F_2$ which is present in the line the analysis of which follows next. Examination of this line showed that it is a single line with no trace of structure in it. Hence it is possible and perhaps reasonable to assume that both the upper and lower terms of this line are single. If this conclusion be correct it will help in the analysis of the next line which is very weak and incompletely resolved

$$\lambda 3048\cdot36 \quad (4d^3F_2 - 4f^3F_2).$$

This line, as remarked above, is extremely weak and difficult to analyse. One broad patch followed by a very weak and hazy one degrading in intensity to the violet is all that is observable. Hence it will be appreciated that only an attempt can be made to analyse such a line. The total width of this line or this patch is 234 units. Since $4f^3F_2$ is very narrow as is reasonable to guess from the examination of the line $\lambda 4431\cdot73 \quad (4d^3D_1 - 4f^3F_2)$, discussed above, the structure of this line is due to the lower term. And by comparing it with the structure of the line $\lambda 3058\cdot08 \quad (4d^3F_2 - A)$, it is perhaps safe to conclude that this patch represents the unresolved first two components expected to be observed in this line.

$$\lambda 3003\cdot93.$$

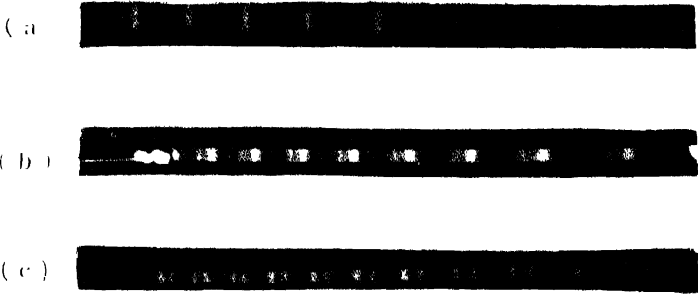
This line has not been classified. It shows a fairly well resolved triplet degrading to the violet.

$$\lambda 2959\cdot70.$$

This is another unclassified line. It is observed as an intensely strong and well resolved triplet degrading in intensity and intervals to the red. The intervals are 256 and 190. As the components degrade to the red the triplet therefore is inverted.

$$\lambda 2465\cdot05.$$

This line is also unclassified. It shows very marked broadening and there is no resolution. It is very weak in intensity. The total width of this line is 235 units.



- (a) Singlet structure shown by the line 4434.73 $4d\ ^3D_1 - 4f\ ^3F'_2$.
- (b) Inverted triplet structure shown by the line 2959.70 degrading to the red.
- (c) Doublet structure shown by the line 2896.21 $4d\ ^3P_0 - D$

It may be noted here that although simple AsII lines, the analysis of which will be found elsewhere, have generally followed the interval and intensity rules fairly accurately this could not be tested in the case of complex lines, since Fisher and Goudsmit's method of analysis involves the assumption that the interval rules are strictly followed. In the ultra-violet region below $\lambda 2500$ the AsII lines are mostly very weak. The region $\lambda\lambda 2800-1800$ has not yet been analysed. Above this region some of the strong lines showing hyper-fine structure have only been partially allocated. The term structures of such lines have therefore only been estimated.

In table I is given a list of the lines studied in this investigation with the observed fine-structures recorded and measured in the ultra-violet region of the spectrum. The strongest component of each line is taken as the main or null line and the separations of the remainder are given as usual, in units of $\text{cm}^{-1} \times 10^{-3}$. The visually estimated intensities are also given below each component in brackets. Structures are classed as A, B and C according to whether resolution is good, medium or poor. The poorly observed components in class C are mostly blurred patches arising probably from the crowding together of fine structure components.

TABLE I

Wave-length	Intensity	Classification of lines	Structures, $\text{cm}^{-1} \times 10^{-3}$	Class
4131.73	10	$4d^3D_1 - 4f^3F_2$	Singl	A
3116.03	10	$4d^3F_3 - B$	9 (5) 190 (4) 340 (2) 545 (3)	A
3058.08	9	$4d^3F_2 - A$	0 (6) 243 (4) 436 (2) 583 (1)	A
3053.46	9	$4d^3F_2 - 4f^3F_3$	76 (1) 0 (8) 113 (2) 178 (6) 297 (5) 361 (3)	B
3048.36	4	$4d^3F_2 - 4f^3F_2$	0 234	
3003.03	8		0 (6) 198 (4) 340 (2)	A
2959.70	10		455 (2) 256 (4) 0 (6)	A
2890.21	6	$4d^3F_3 - D$	0 (3) 262 (2)	B
2884.51	8	$4d^3F_3 - E$	0 (3) 271 (2)	B
2830.45	8	$4d^3F_3 - F$	0 (3) 259 (6)	B
2465.65	3	...	0 235	C

of a complex line which takes place when the structures in the upper and lower terms of a line are small and of similar order. One of the lines, as will be seen from the table, has shown an inverted structure, that is, its components are found degrading to the red. The line with a complex structure has been analysed by the graphical method of Fisher and Goudsmit (*loc. cit.*). The structures and interval factors of the various terms are given in table II.

TABLE II
Term Fine Structures and Term Interval Factors

Terms.	Fine structure intervals			Term interval factors.
	Small			Small
$\left\{ \begin{array}{l} 3D_1 \\ 4d \quad 3F_3 \\ 3F_2 \end{array} \right.$	370	210	150	60
	252	180	108	72
$\left\{ \begin{array}{l} 3F_3 \\ 4f \quad 3F_2 \end{array} \right.$	81	93	45	18
	Small			Small

ACKNOWLEDGMENTS

The writer wishes to express his thanks to Professor O. W. Richardson, F.R.S., Nobel Laureate, in whose laboratories at King's College, London, this investigation was carried on, and to Dr. W. E. Williams for his help and the excellent facilities he provided during the course of this work.

REFERENCES.

- ¹ *Proc. Roy. Soc.*, 137-541 (1932) and *Zeit. f. Phys.*, **87**, 210 (1938).
- ² *Zeit. f. Physik*, **84**, 236 (1933).
- ³ Mukerji, *Ind. J. Phys.*, **11**, 123 (1937).
- ⁴ *Ind. J. Phys.*, **7**, 561 (1933).
- ⁵ *Phys. Rev.*, **37**, 1341 (1931).
- ⁶ Mukerji, *Ind. J. Phys.*, **11**, 377 (1938).
- ⁷ *Loc. cit.*
- ⁸ Paschen, *Sitz. d. Preuss. Ak. Wiss.*, **32**, 502 (1932); Schuler and Jones, *Zeit. f. Physik*, **77**, 811 (1932).

DISPERSION, ABSORPTION AND POLARISATION CURVES FOR RADIO WAVE PROPAGATION IN THE IONOSPHERE *

By SARAJU PRASAD GHOSH, M.Sc.,
Sir Rashbehary Ghose Research Scholar in Physics,
University of Calcutta.

(Received for publication, September 24, 1938.)

ABSTRACT Dispersion, absorption and polarisation curves for radio wave propagation in the ionosphere for frequencies (3.0, 1.27, 1.6 megacycles) and for collisional frequencies (10^6 , 5.4×10^6 , 10^7) are drawn on the basis of the magneto-ionic formulae of Appleton and Hartree for the magnetic condition of the upper atmosphere at Calcutta (total intensity 0.452 gauss, dip $31^\circ 45' N$). In connection with the state of polarisation of the downcoming waves the case of limiting polarisation is discussed. It is shown that contrary to the view held by some authors, the polarisation of the two split components on their emergence from the ionosphere will, in general, be elliptical. This latter view confirms the experimentally obtained results regarding the nature of limiting polarisation.

I. INTRODUCTION

The theory of propagation of electromagnetic waves through a conducting medium under the influence of a magnetic field has been developed by Appleton¹ and later on by Hartree² and also by Goldstein. According to these authors the relations between the refractive index μ , absorption coefficient k and the polarisation R are given by

$$c^2 q^2 = (\mu - i\chi)^2 = 1 + \frac{1}{(a + i\beta) - \frac{\gamma_T^2}{2(1 + a + i\beta)}} \pm \sqrt{\left[\frac{\gamma_1^4}{4(1 + a + i\beta)^2} + \gamma_L^2 \right]} \dots (1)$$

$$R = \frac{H_x}{H_y} = \frac{1}{i\gamma_L} \left[\frac{1}{c^2 q^2 - 1} - a - i\beta \right] \dots (2)$$

where

$$\chi = \frac{ck}{p}$$

* Communicated by the Indian Physical Society.

$$\alpha = -\frac{p^2}{p_0^2} - \frac{1}{3}, \quad \beta = \frac{pv}{p_0^2}$$

$$\gamma_L = \gamma \cos\theta, \quad \gamma_T = \gamma \sin\theta$$

in which

$$p_0^2 = \frac{4\pi N e^2}{m}, \quad \gamma = \frac{hp_u}{p_0^2}, \quad p_R = \frac{Hc}{mc}$$

and m, e = mass and charge respectively of an electron

N = electron density

H = intensity of the earth's magnetic field

θ = angle between H and the direction of propagation

p = angular frequency of the propagated waves

v = frequency of collision of an electron with gas molecules.

Equations (1) and (2) show that in general, for any direction of propagation in such a medium two waves of different phase velocities, different absorption coefficients and different polarisations are propagated. It should be mentioned that these equations were developed in connection with investigations on the propagation of radio waves through the ionosphere which, owing to the presence of electrons and ions, behaves like a conductor and is at the same time subject to the influence of the magnetic field of the earth. The same formulae have been obtained by different methods of attack by Saha and Rai³ and also by Bose.⁴ Special mention might be made of the analysis of the last named author who starting from the microscopic equations of Lorentz, has obtained the conditions of total reflection taking the damping due to collisions into account, which plays an important part in the propagation phenomenon.

The general properties of the above formulae and the various types of dispersion, absorption and polarisation curves they yield, have been studied by various authors. Unfortunately, for reasons described below, none of these curves can be utilised for conditions of the ionosphere at Calcutta. Amongst the authors who have studied the dispersion formulae, mention might be made of Ratcliffe,⁵ Taylor⁶, Booker⁷, Bailey, Martyn⁸ and Goubau.⁹ Ratcliffe has discussed the simple case when $v=0$. Taylor has made elaborate calculations and drawn a large number of typical curves taking the damping effect into account. But she has included the Lorentz term¹⁰ in the expression for α , i.e., she has taken

$$\alpha = -\frac{p^2}{p_0^2} - \frac{1}{3}.$$

Martyn has also drawn dispersion curves by utilising an elegant graphical method due to Bailey, but he has also included the Lorentz term. We now know, however, from a recent analysis by Darwin¹¹ that for conditions prevailing

in the ionosphere the Lorentz term ought to be omitted. Goubau's curves, though drawn omitting the Lorentz term, are for the value of the magnetic field in Germany. We thus see that the dispersion curves of none of these authors can be utilised either because they include the Lorentz term (1) or because they are drawn for a value of the magnetic field which is much different from that at Calcutta.* In the present paper therefore, dispersion, absorption and polarisation curves for Calcutta condition, neglecting the Lorentz term have been drawn, so that they may be used by the ionospheric investigators in this country.

It should be mentioned here that besides the dispersion curves there is another type of curves the delineation of which is also important for proper interpretation of "reflection" of waves in the group retardation method of ionospheric investigation. This latter type of curves depicting the variation of group velocity with electron density has been drawn by Goubau¹⁴ and also by Bajpai and Mathur.¹⁵ Unfortunately, however, the curves actually drawn are not of much practical value (except that they bring out the fourth condition of reflection) because in drawing them the damping factor has been neglected. Such simplification would obviously lead to erroneous results since the effect of damping becomes specially important near the point of reflection. The group velocity curves, if drawn with the help of more complete formula taking collision into account, would undoubtedly be of great help in elucidating the propagation phenomenon of radio waves in the ionosphere.

The method employed for drawing these curves is that of conformal representation suggested by Bailey.¹⁰ For the sake of completeness the method with minor modifications is summarised below.

2. POLARISATION

From equations (1) and (2) we have, after eliminating $(c^2q^2 - 1)$,

$$R + \frac{i\gamma_T^2/\gamma_L}{1 + \alpha + i\beta} = \frac{2}{\alpha + i\gamma} \quad (3)$$

* There has very recently been a recrudescence of the controversy with regard to the inclusion or otherwise of the Lorentz polarisation term (1). Martyn and his associates¹² in Australia think that they have got definite experimental proof in favour of exclusion of the Lorentz term. American workers, Booker and Berkner¹³ on the other hand, give a different interpretation to the experimental observations of the Australian workers and analysing the records of their own observations maintain that the Lorentz term should be retained. It seems that the only possible way of deciding between these two hypotheses is to make experimental study of the polarisation of echoes for frequencies less than the gyro-frequency.

We have thought fit to exclude the Lorentz term in accordance with the theoretical work of Darwin.

where

$$x = \frac{\sigma v}{p_n}, \quad y = \frac{\sigma p}{p_n} \left(1 - \frac{p^2}{p^2} \right) \quad \dots (4)$$

and

$$\sigma = 2 \cos \theta / \sin^2 \theta.$$

Let us now put,

$$Z = x + iy, \quad \xi = \xi + i\eta = Z^{-1}, \quad R = \rho e^{-i\phi} = e^{i\omega} \quad \dots (5)$$

where $\rho > 0$, $\omega = u + iv$

and $x, y, \eta, \rho, \phi, u$ and v are all real.

Let us represent ω and Z conformally in the ξ -plane.

It can be shown that the u -curves and the v -curves are respectively given by the following confocal hyperbolas and ellipses .

$$\xi^2 / \cos^2 u - \eta^2 / \sin^2 u = 1 \quad \dots (6)$$

$$\xi^2 / \cosh^2 v + \eta^2 / \sinh^2 v = 1 \quad \dots (7)$$

with their foci on the ξ -axis at the point $\xi = \pm 1$ and the asymptotes of (6) are the lines $\eta = \pm \tan u$.

Moreover, since $R = \rho e^{-i\phi} = e^{i\omega} = e^{-v} e^{iu}$

$$\rho = e^{-v} \quad \text{and} \quad \phi = -u.$$

If a, b respectively denote the semi-major and semi-minor axes of the ellipse (7), it can be shown that

$$\left. \begin{aligned} \rho_1 &= a - b, & \phi_1 &= -u \\ \rho_2 &= a + b, & \phi_2 &= +u \end{aligned} \right\} \quad \dots (8)$$

Since the semi-axes are essentially positive quantities, v is always positive.

For convenience the following important property of confocal ellipses and hyperbolas is used .

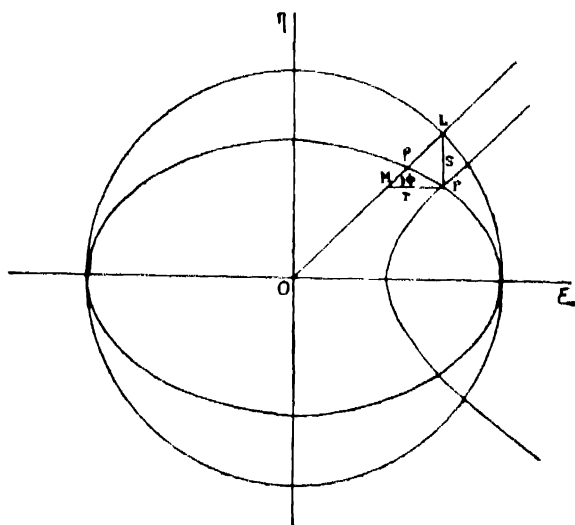


FIG. 1.

Let P (Fig I) be the point of intersection of the hyperbola (6) and the ellipse (7). Draw PL, parallel to the η -axis, cutting the asymptote to the hyperbola at L; then L lies on the auxiliary circle of the ellipse. If PM is drawn parallel to the ξ -axis, cutting OL, at M, then

$$LM = a - b$$

and

$$\angle LMP = -u = \phi_1$$

Now, it follows from equations (5) that the x -curves and the y -curves are respectively given by the following system of coaxial circles :

$$\xi^2 + \eta^2 = x^{-1}\xi \quad \dots \quad (9)$$

$$\xi^2 + \eta^2 = -y^{-1}\eta \quad \dots \quad (10)$$

The circles (9) with their centres on the ξ -axis, have their diameters equal to x^{-1} and all pass through the origin. The circles (10) form a similar system with their centres on the η -axis.

Thus finally to determine polarisation, first of all, the values of x and y are calculated by means of (4). Next the circles with diameters equal to x^{-1} and y^{-1} are drawn. Since the ellipse and hyperbola giving ρ_1, ρ_2, ϕ_1 and ϕ_2 must pass through the point of intersection of these circles, we at once get the point P. Moreover, as the foci are at $\xi = \pm 1$, the auxiliary circle of the ellipse is easily drawn and the points L, and M are located, thus obtaining

$$\left. \begin{aligned} LM &= a - b \\ \angle LMP &= \phi_1 \end{aligned} \right\} \quad (11)$$

Representing polarisation after Taylor, we have,

$$\begin{aligned}\tan\theta &= i \frac{E_{\parallel}}{E_{\perp}} = -i \frac{H_{\perp}}{H_{\parallel}} \\ &= -i\rho e^{-i\psi} \\ &= -i\rho \cos\psi - \rho \sin\psi \\ &= A + iB\end{aligned}$$

where

$$A = -\rho \sin\psi$$

$$B = -\rho \cos\psi$$

It can be shown that if ψ denotes the inclination of the polarisation ellipse to the axis of Z, then

$$\tan 2\psi = \frac{-2\rho \cos\psi}{1 - \rho^2} \quad \dots (12)$$

and

$$\tan^2\theta = \frac{(1 + \rho^2) \sin 2\psi + 2\rho \cos\psi}{(1 + \rho^2) \sin 2\psi - 2\rho \cos\psi} \quad \dots (13)$$

The sign of ψ is determined by the sign of B ($= -\rho \cos\psi$) ; if $B < 0$, as is usually the case with the ordinary wave, ψ is a negative acute angle.

The sign of θ is determined by that of A ($= -\rho \sin\psi$).

(i) when ψ is $+ve$

$$A < 0$$

and the rotation is clock-wise or right-handed (when viewed along the positive direction of propagation of the waves) ; whereas

(ii) when ψ is $-ve$

$$A > 0$$

and the rotation is anti-clockwise or left-handed. Thus if positive value of θ corresponds to right-handed polarisation, we have finally,

$$\begin{array}{l} \text{when} \quad \left. \begin{array}{ll} \psi \text{ is } +ve, & \theta \text{ is } +ve \end{array} \right\} \\ \text{and} \quad \left. \begin{array}{ll} \psi \text{ is } -ve, & \theta \text{ is } -ve \end{array} \right\} \end{array} \quad \dots (14)$$

Moreover, it is obvious that $\theta = 0$ corresponds to linear polarisation and $\theta = \pm 45^\circ$ corresponds to right- or left-handed circular polarisation respectively.

Let us denote the polarisation of the ordinary and the extraordinary mode of propagation by the subscripts o and x respectively, so that from (8),

$$\phi_o = -\phi_x \quad \text{and} \quad \rho_o = \rho_x^{-1}$$

The sign of ϕ_o depends upon the quadrant in which the angle is found (in the 1st quadrant u is $-ve$ and hence ϕ_o is $+ve$), while ρ_o is always less than unity.

3. REFRACTIVE INDEX AND ABSORPTION COEFFICIENT

The calculation of μ and χ $\left(\frac{ck}{p}\right)$ now becomes simple as can be seen from the following.

Equation (2) can be written as

$$(\alpha + i\beta + iR\gamma_L)\{[\mu - i\chi]^2 - 1\} = 1 \quad \dots (15)$$

We may put

$$\begin{aligned} R &= \rho e^{-i\phi} \\ &= r - is \end{aligned}$$

where

$$r = \rho \cos \phi, \quad s = \rho \sin \phi$$

The values of r and s can be obtained from Fig. 1, where,

$$r = PM \quad \text{and} \quad s = PL$$

$$\text{Putting} \quad X = \alpha + s_L, \quad Y = \beta + r\gamma_L, \quad \xi = \mu^2 - \chi^2 - 1, \quad \eta = -2\mu\chi \quad \dots (16)$$

it will be seen that the μ -curves and the χ -curves are respectively given by the parabolas

$$\eta^2 = 4\mu^2 (\mu^2 - 1 - \xi) \quad \dots (17)$$

$$\eta^2 = 4\chi^2 (\chi^2 + 1 + \xi) \quad \dots (18)$$

with their axes on the axis of ξ and common focus at the point $(-1, 0)$. It is clear that the χ -curves are the exact images of the μ -curves in the line $\xi = -1$ and so need not be drawn.

Thus to find μ and χ , r and s are obtained from figure 1; then X and Y are calculated by means of (16) and the corresponding circles are drawn. The parabola (17) giving the required value of μ^2 must pass through the point of intersection of these circles. After obtaining μ the calculation of χ becomes clear.

4. DESCRIPTION OF THE CURVES

The curves have been drawn for the case of vertical propagation of waves of three typical wave-lengths (100m, 2357m, 500m) and for four values of the collisional frequencies ($0, 10^6, 5.1 \times 10^6, 10^7$). Corresponding to the earth's

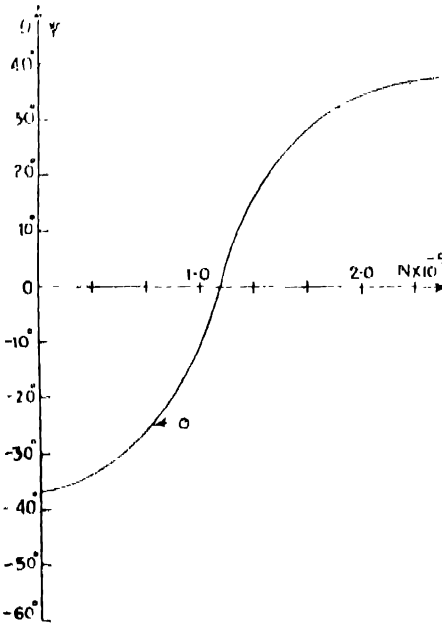


Fig. 2(a) $\lambda = 100 \text{ m}, \nu = 0$

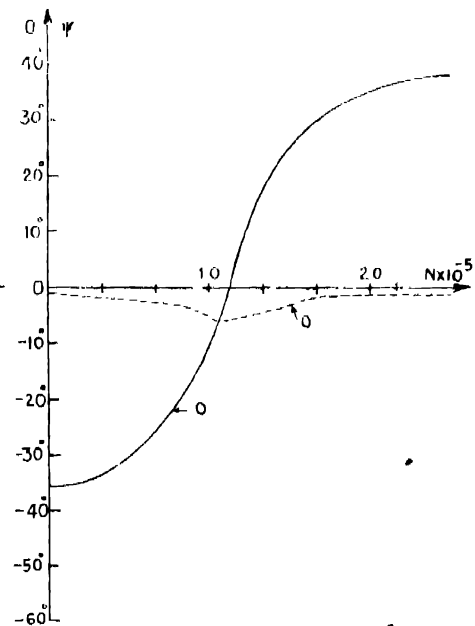


Fig 2(b) $\lambda = 100 \text{ m}, \nu = 10^6 < \nu_c$

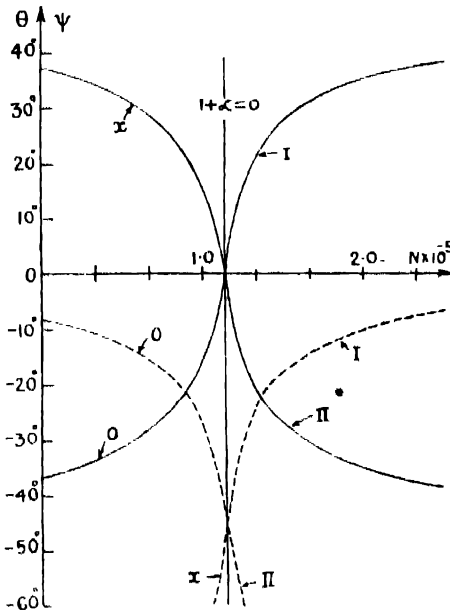


Fig. 2 (c) $\lambda = 100 \text{ m}, \nu = \nu_c$

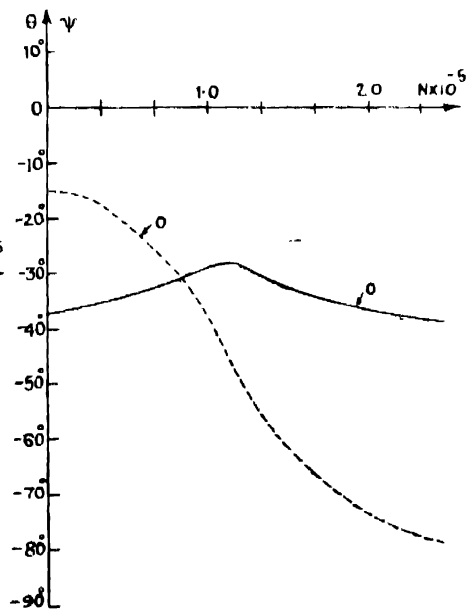


Fig. 2(d) $\lambda = 100 \text{ m}, \nu = 10^7 > \nu_c$

magnetic field (0.452 gauss) and the dip ($31^{\circ}45'$ N) at Calcutta, the value of the critical collisional frequency $\nu_c (= p\tau^2/2p_L)$ is 5.4×10^6 per sec and the gyromagnetic wave-length $\lambda_H = 235.7$ m. The polarisation, dispersion and absorption curves given in Figs. 2 to 7 illustrate clearly the effect of damping due to the collision between electrons and the neutral gas molecules upon the propagation

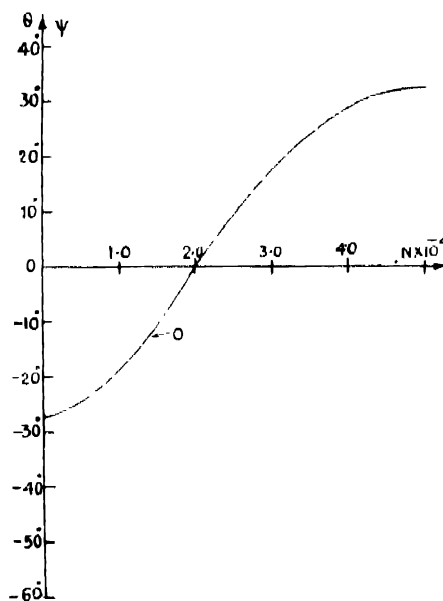


Fig.3(a) $\lambda = 235.7$ m, $\nu = 0$

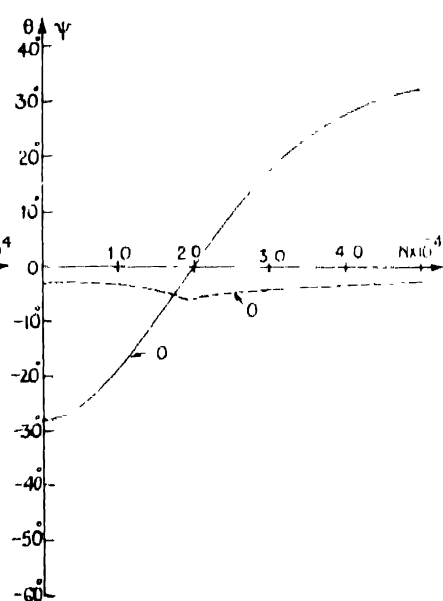


Fig.3(b) $\lambda = 235.7$ m, $\nu = 10^6 < \nu_c$

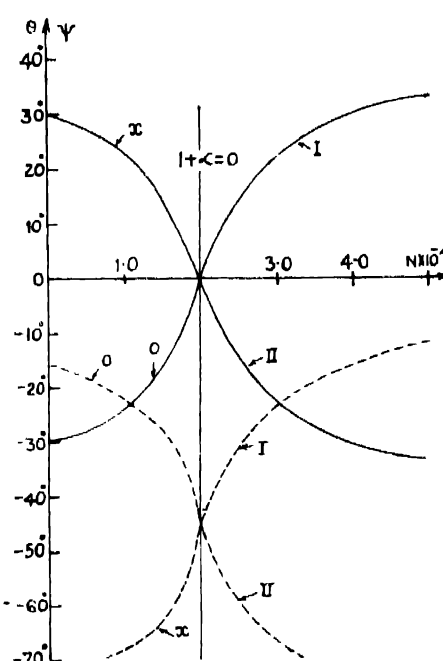


Fig.3(c) $\lambda = 235.7$ m, $\nu = \nu_c$

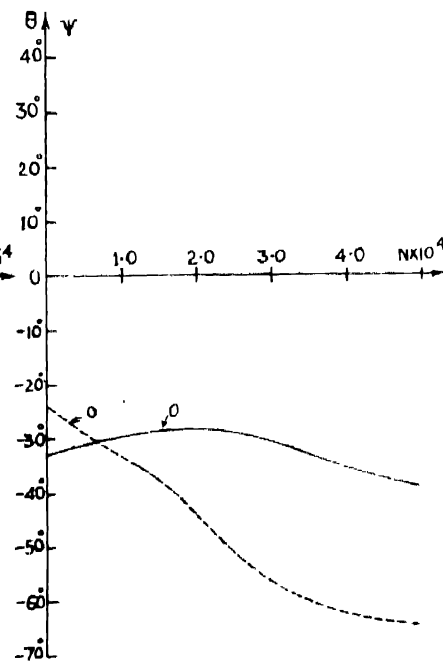


Fig.3(d) $\lambda = 235.7$ m, $\nu = 10^7 < \nu_c$

phenomenon. As already pointed out, the curves corresponding to the ordinary component of the split waves are marked as 'o' while those for the extraordinary component by 'x'. Moreover, the full-line curves represent μ and θ and the broken line curves give χ and ψ .

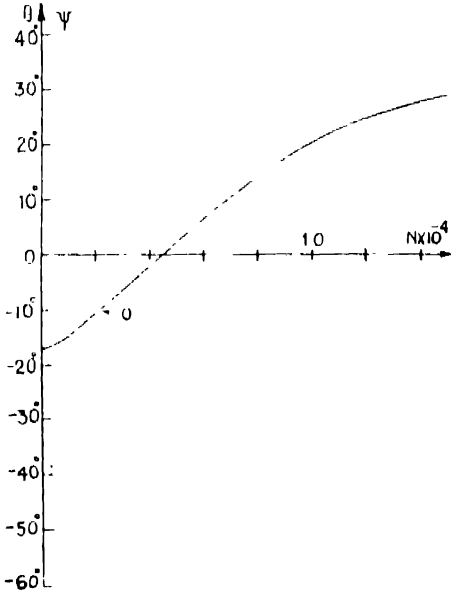


Fig 4(a) $\lambda = 500 \text{ m}$, $\nu = 0$

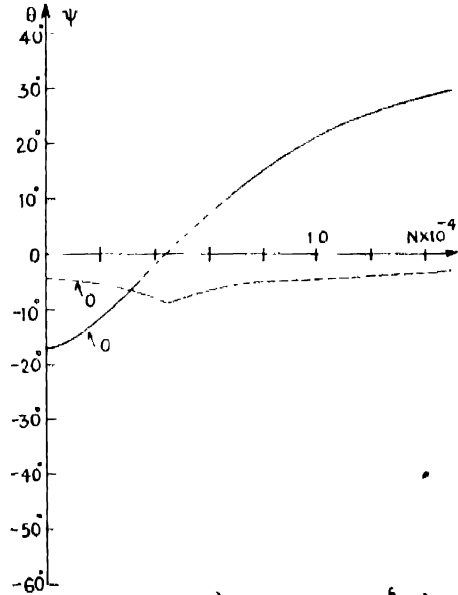


Fig 4(b) $\lambda = 500 \text{ m}$, $\nu = 10^6 < \nu_c$

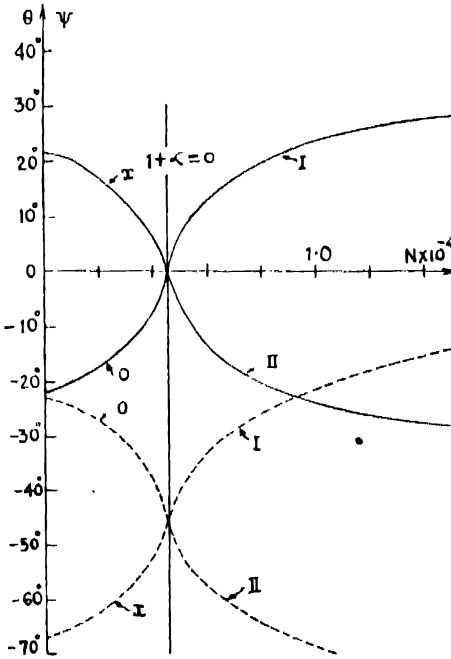


Fig 4(c) $\lambda = 500 \text{ m}$, $\nu = \nu_c$

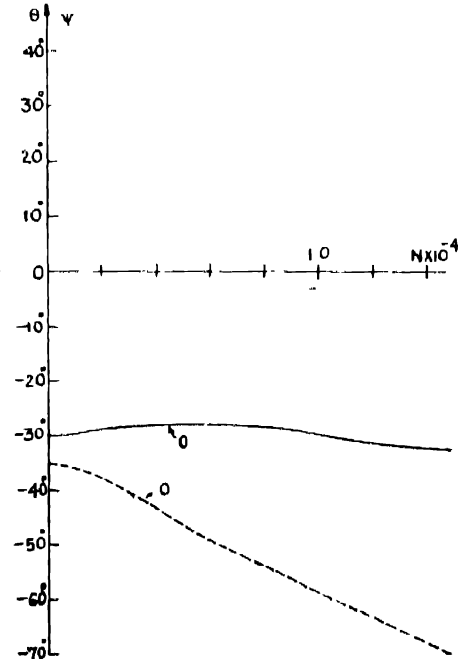


Fig.4(d) $\lambda = 500 \text{ m}$, $\nu = 10^7 > \nu_c$

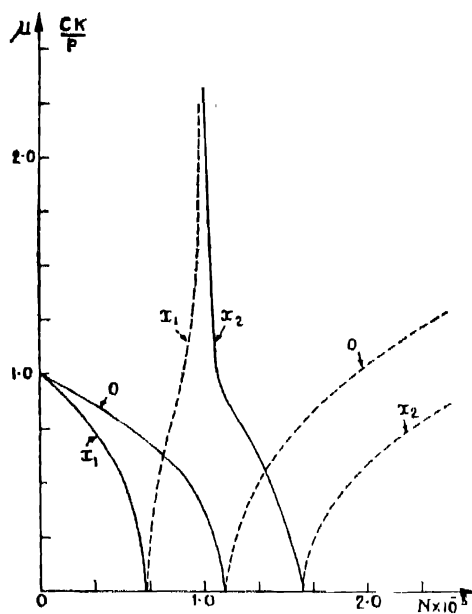


Fig. 5(a) $\lambda = 100$ m, $\nu = 0$

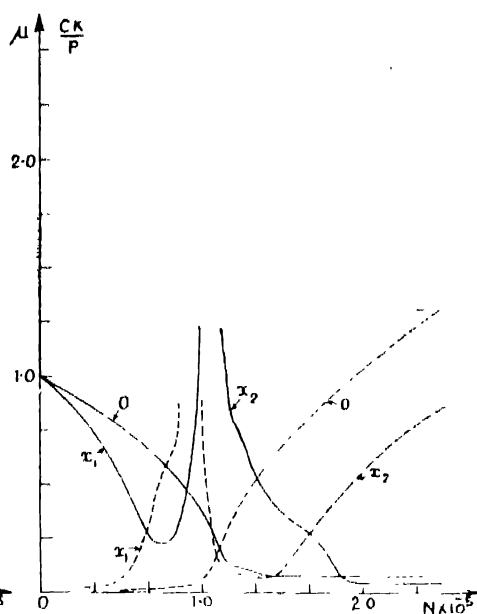


Fig. 5(b) $\lambda = 100$ m, $\nu = 10^6 < \nu_c$

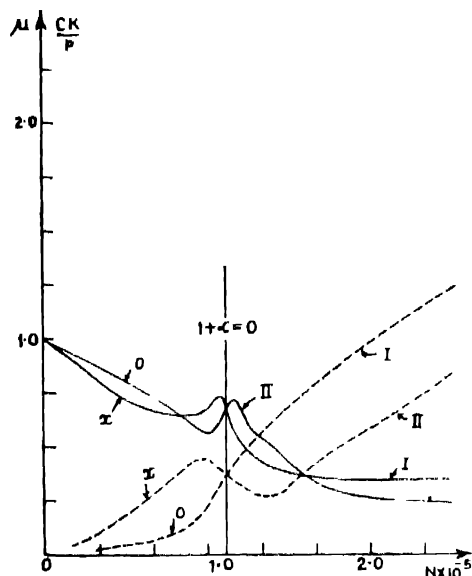


Fig. 5(c) $\lambda = 100$ m, $\nu = \nu_c$

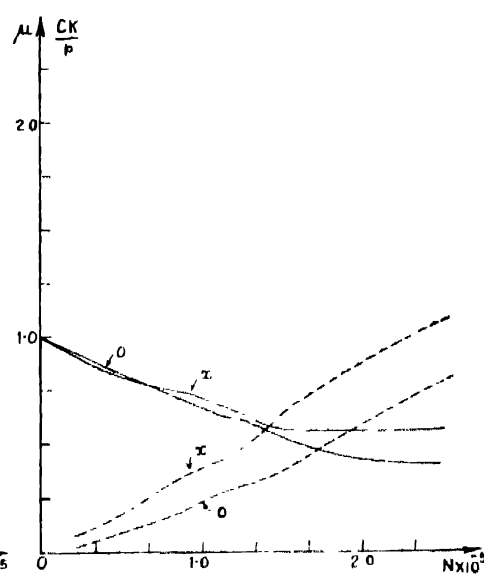


Fig. 5(d) $\lambda = 100$ m, $\nu = 10^7 > \nu_c$

5. DISCUSSION

(Limiting Polarisation)

A general discussion of the dispersion, absorption and polarisation curves has been given by Taylor. There is however, a point of difference between ours and Taylor's results regarding the limiting values of θ and ψ (the polarisation

and the tilt of the polarisation ellipse respectively) as N —the electron density tends to zero, which deserves consideration. According to Taylor θ and ψ have the values 45° and 0° for $N=0$. It will be seen from the figures that in our calculation, θ and ψ tend to limiting values other than those given by Taylor, as $N \rightarrow 0$. This has also been obtained by Martyn who supports his results from experi-

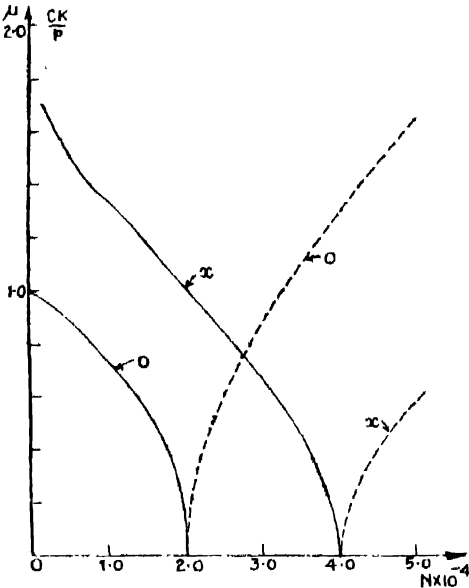


Fig. 6(a) $\lambda = 235.7 \text{ m}$, $\nu = 0$

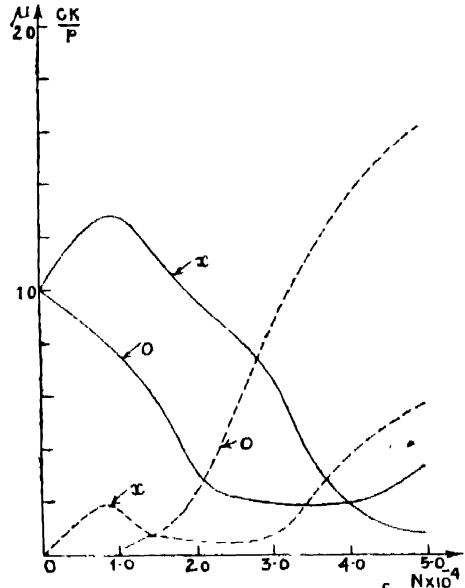


Fig. 6(b) $\lambda = 235.7 \text{ m}$, $\nu = 10^6 \angle \nu_c$

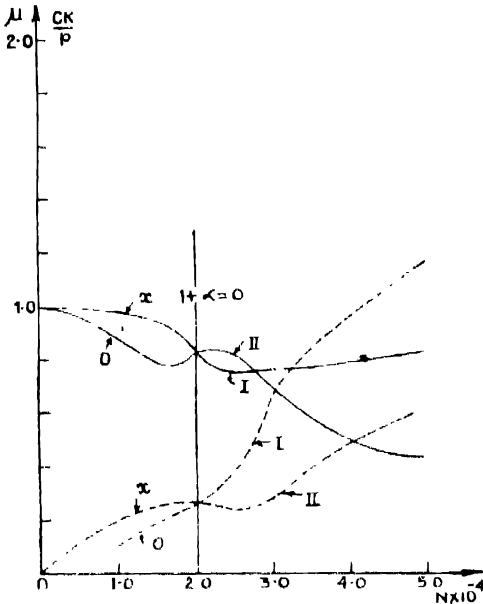


Fig. 6(c) $\lambda = 235.7 \text{ m}$, $\nu = \nu_c$

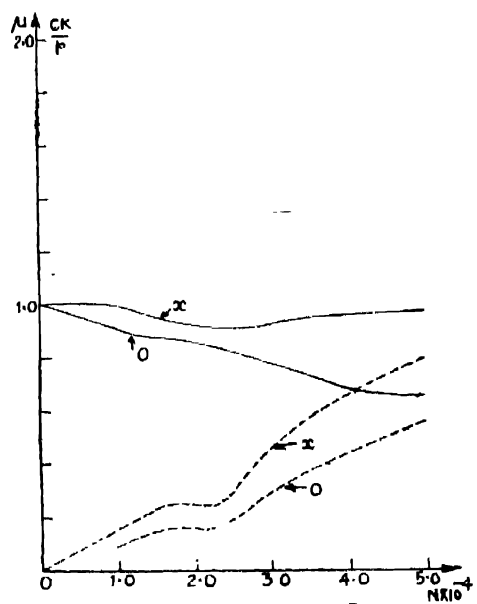


Fig. 6(d) $\lambda = 235.7$, $\nu = 10^7 > \nu_c$

mental observations of Baker and Green.¹⁶ In support of the limiting values of θ and ψ (45° and 0°) depicted by Taylor, in her polarisation curves, she states that the Appleton-Hartree formulæ are inapplicable when N tends to zero. She has therefore merely assumed that the waves on entering the ionosphere should split up into two oppositely circular-polarised waves and has delineated this in her curves by extrapolation. We are not however justified in assuming that the

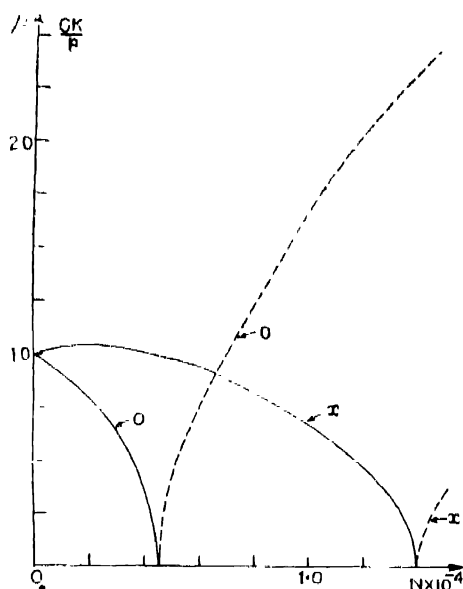


Fig. 7(a) $\lambda = 500$ m. $\nu = 0$

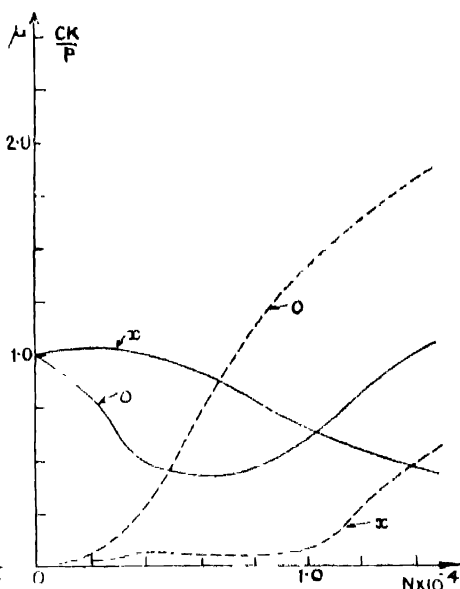


Fig. 7(b) $\lambda = 500$ m. $\nu = 10^6 < \nu_c$

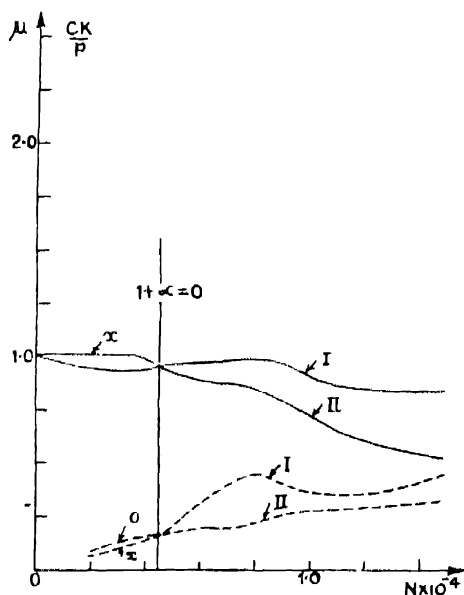


Fig. 7(c) $\lambda = 500$ m. $\nu = \nu_c$

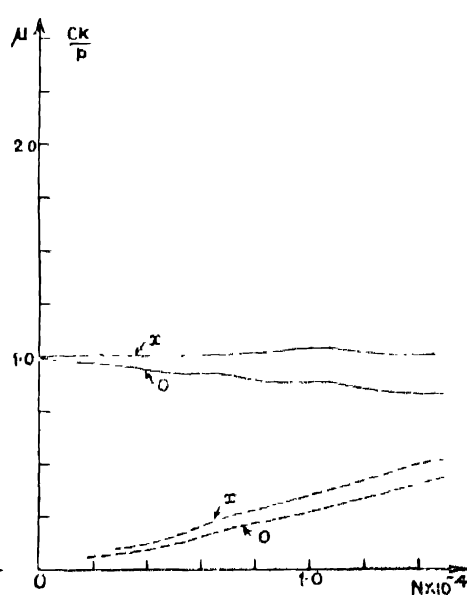


Fig. 7(d) $\lambda = 500$ m. $\nu = 10^7 > \nu_c$

waves should be split up into two oppositely circular-polarised components except in the special case when the wave is travelling along the direction of the magnetic field. If the wave normal is inclined to the magnetic field, then on entering the ionosphere the split waves should be elliptically polarised. The waves, if they could retrace their paths, would also on emergence be elliptically polarised. This is exactly what our calculations show for the case of limiting polarisation.

ACKNOWLEDGMENT

The investigation was undertaken at the suggestion of Prof. S. K. Mitra to whom I express my sincere thanks for constant help and guidance. I also take this opportunity of thanking Dr. H. Rakshit for many helpful discussions during the progress of the work.

WIRELESS LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE,
92, UPPER CIRCULAR ROAD,
CALCUTTA.

REFERENCES

- ¹ Appleton, *Journ. Inst. Elec. Eng.*, **71**, 642 (1932).
- ² Hartree, *Proc. Camb. Phil. Soc.*, **25**, 47 (1929).
- ³ Saha and Rai, *Proc. Nat. Inst. Sci. India*, **3**, 359 (1937).
- ⁴ Bose, *Ind. Jour. Phys.*, **12**, 121 (1938).
- ⁵ Ratcliffe, *Wir. Eng. and Expt. Wir.*, **10**, 354 (1933).
- ⁶ Taylor, *Proc. Phys. Soc.*, **46**, 408 (1934).
- ⁷ Booker, *Proc. Roy. Soc. A*, **147**, 352 (1934).
- ⁸ Martyn, *Phil. Mag.*, **19**, 376 (1935).
- ⁹ Goubau, *H.F.T.*, **45**, 179 (1935).
- ¹⁰ Bailey, *Phil. Mag.*, **18**, 516 (1934).
- ¹¹ Darwin, *Proc. Roy. Soc. A*, **146**, 17 (1934).
- ¹² Martyn and Munro, *Nature*, **141**, 159 (1938).
- ¹³ Booker and Berkner, *Nature*, **141**, 562 (1938).
- ¹⁴ Goubau, *H.F.T.*, **44**, 17 (1934).
- ¹⁵ Bajpai and Mathur, *Ind. Jour. Phys.*, **11**, 165 (1937).
- ¹⁶ Baker and Green, *Report No. 3 Commonwealth Radio Research Board, Bulletin 60, Australian Coun. Sci. and Indust. Res.* (1932).

THE ORIGIN OF NEW LOW-FREQUENCY RAMAN LINES IN SOLIDS

By JAGANNATH GUPTA.

(Received for publication, 24th September, 1938.)

Plate X.

ABSTRACT. Following a previous communication on the subject, observations with the Raman spectra of tartaric acid, sodium tartrate and benzophenone crystals have been recorded, which go against the possibility of the new lines being due to lattice oscillations. The specific heat values of carbon disulphide at low temperatures have been found to agree closely through a long range of temperatures with those derived from the new frequencies of the substance in the solid state, by taking these as Einstein and not Debye frequencies.

INTRODUCTION.

In a previous paper,¹ experimental evidences and simple considerations of polarisability changes were summarised to point out that there are serious difficulties in attributing the origin of the new Raman lines observed close to the Rayleigh line in many solids, to vibrations of the lattices. With *p*-dichlorobenzene, the positions of the new Raman lines were found to change even when the crystal structure remained the same: while with *cis* and *trans* dichloroethylenes, having presumably different crystal structures, the new lines were observed in the same position. It was also pointed out² how the selection rule for lattice oscillation in Raman effect³ cannot account for even the appearance of the new lines in the spectrograms of many crystals, much less their observed high intensities (which very often compare with, and sometimes exceed the intensities of the most intense vibrational lines of the substances), if they are taken to be due to lattice oscillations. This latter point has been pursued further (*a*) by examining the Raman spectra of a few other substances in the crystalline state, the results of which are described in section A of the present paper, and (*b*) by comparing the total contribution of these new frequencies to specific heat, assuming them to be due to lattice oscillations first, with the same observed for these substances at low temperatures (where Einstein contributions due to intramolecular frequencies

become insignificant). The results for carbon disulphide, embodied in section B of the present paper, clearly show that the new lines observed in the solid state cannot be treated as due to lattice oscillations

§ A.

A course of investigation on the Raman spectra of crystalline substances, having different crystal symmetries, has been taken up using large single crystals, with a view to studying any notable changes in the positions and character of the intramolecular Raman lines recorded for these substances in other states, and more particularly to recording any new lines in the region of $(20-200) \text{ cm}^{-1}$ s from the Rayleigh line. The vibration spectra of tartaric acid, sodium tartrate and benzophenone have been obtained and the nature of changes have been indicated. It has also been observed that with the crystal of sodium tartrate, no new line close to the Rayleigh line of any appreciable intensity has been recorded; while with the crystal of the acid, there are sharp and intense lines. The molecular crystal of benzophenone also shows the presence of new lines.

EXPERIMENTAL.

Large, transparent crystals of sodium tartrate, tartaric acid and benzophenone were chosen. They were not true single crystals, in the crystallographic sense, and the faces were ill developed. Plane faces perpendicular to each other were artificially developed by rubbing the crystals on a piece of cloth moistened with liquids in which the substances are freely soluble, water being used for the acid and its sodium salt, and benzene for benzophenone.

A Heraeus quartz mercury arc lamp was placed in the end-on position and light emerging from the plane quartz window at one end was accurately focussed on the crystal with the help of a small convex lens. The face of the crystal nearest to, and facing the slit of the spectrograph, through which the scattered light was received on the slit, was partly screened with a piece of black paper, leaving a rectangular aperture in the middle, to avoid parasitic light. The back surfaces were completely screened by sticking pieces of non-reflecting black paper.

The crystals were very thinly covered with a layer of transparent, colourless* vaseline, to preserve the faces from decrepitation due to evaporation, dehydration, or absorption of moisture. Considerable accuracy in alignment was necessary to avoid light reflected inside the crystals. The spectrograms are reproduced in Plate X, and the results are given with those by previous workers, obtained with either solutions or in the liquid state, in table I.

TABLE I.

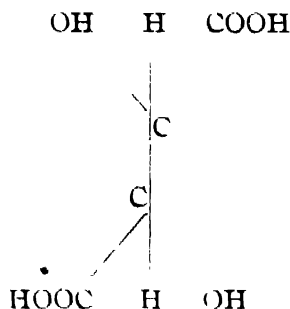
Raman lines in cm^{-1} s. Figures in parentheses indicate relative intensities.

Tartaric acid		Sodium tartrate		Benzophenone	
Crystal.	Solution in water.	Crystal.	Solution in water.	Crystal.	Molten
36(2)					
80(1)				49(3)	
103(1)				95(1)	
124(2)				147(1)	148(9b)
				169(1)	
	367(3)		378(1b)	218(4)	219(10)
					286(4)
	517(3)		532(2b)	562(2)	403(4)
	601(2)		618(1b)	617(3)	564(6)
					615(7)
	600(2)			721(3)	716(6)
731(3)	751(6)			767(2)	761(5)
840(1)	838(1)	888(2)	805(4)	852(1)	805(1)
					848(3b)
895(1b)	891(5)		893(4)		
	993(3)	990(1)	992(6)	1000(8)	999(15)
	1091(2)	1071(1)	1068(3b)	1027(4)	1026(6)
1141(1)	1140(2)	1118(1)	1121(3b)	1147(6)	1149(10b)
	1279(4vb)	1215(3)	1224(2vb)		1276(5)
			1310(2b)		1313(2)
	1413(1)		1370(5b)		1377(1)
	1442(2)		1418(6vb)	1459(1)	1448(3)
			1617(1vb)	1490(1)	1488(3b)
				1597(15)	1593(12b)
1745(1b)	1740(5b)			1650(10)	1653 $\pm$ 11(10b)
2944(1)	2950(6vb)		2936(8vb)	3055(3)	3063(6b)
2970(2)					

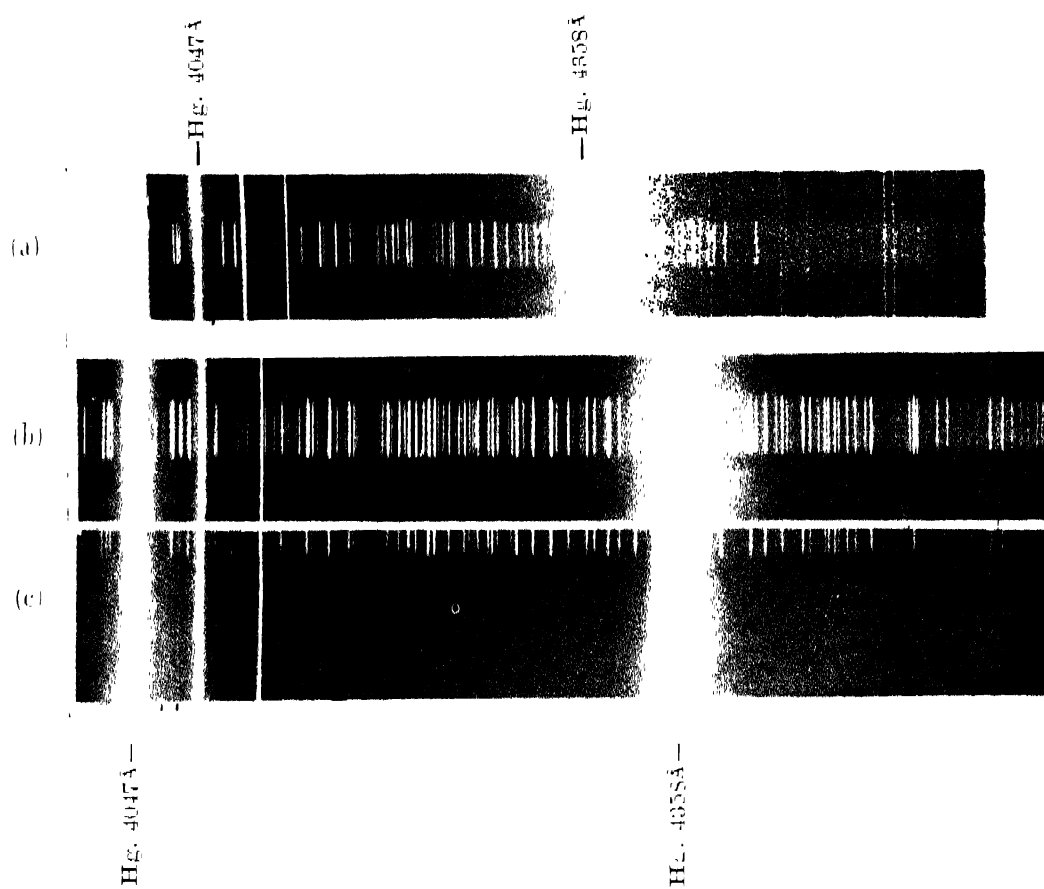
DISCUSSION

It may be observed that, besides a general sharpening in the character of the Raman lines, which is, however, characteristic of the vibration spectra of solids, no very great change in the position of the Raman lines is noticeable in the spectrograms of different states of these substances. While with such complex molecular units, any attempt to trace the nature of molecular deformation at different states is futile, the close similarity between the spectra of the liquid and solid states indicates that these molecules do not undergo any great structural deformations at the different states. Many of the lines observed in the liquid state are apparently missing in the solid state. The reason for this apparent discrepancy is that the Raman spectrum recorded with the crystal is rather feeble, and only those lines which have become a little sharper in the solid state have come out with appreciable intensity, while the broader lines are extremely feeble and are practically masked by the continuous background.

An interesting point to observe is that several new lines close to the Rayleigh line are present in the spectrogram of tartaric acid, but absent in that of sodium tartrate, although the latter is recorded more intensely than the former. The opposite of this would be expected, if these lines were regarded as due to lattice oscillations; because, in the crystal of sodium tartrate, the forces developed during vibrations of the ionic lattice are of comparatively greater magnitude than the molecular lattice of tartaric acid, giving rise to, in the former case, greater asymmetric restoring force, which is known to determine the intensity of lattice oscillations in Raman effect. The arrangement of tartaric acid in the unit cell, described by Bragg, ¹ shows considerable elements of symmetry, besides the fact that the molecule is itself centro-symmetrical, as can be easily seen from the following figure—



The asymmetric restoring force, which is already of a small order of magnitude, the lattice being molecular, is further reduced by the development of these elements of symmetry in the lattice. On comparing between the free acid and the sodium salt of the same acid in the solid state, the selection rule for Raman lines due to lattice oscillations predicts greater intensity of those due to the salt. The contrary fact recorded here, *viz.*, that the new lines have been observed in the



Raman Spectra of Crystals.

- (a) Benzophenone.
- (b) Sodium tartrate.
- (c) Tartaric acid

spectrogram of tartaric acid and not in that of its sodium salt, although the ordinary vibrational lines are recorded in the latter with greater intensities, therefore renders Gross and Vuks's suggestion that the new lines might be due to lattice oscillations, extremely doubtful. It appears, at least in this particular instance, that the new lines observed in the case of tartaric acid are not due to lattice vibrations.

The spectrogram of a molecular crystal of benzophenone also shows similar lines close to the Rayleigh line. The molecule is quite big, being constituted of two flat benzene rings attached to two sides of a carbonyl group, so that angular oscillations of the type postulated by Pauling in simple molecules are not here of any appreciable magnitude, and are therefore not expected to appear as Raman lines of any measurable intensity. On the other hand, while the comparatively large intensity of the line at 49 cm^{-1} is not in favour of the explanation that this might represent a lattice frequency, it requires to be proved that the observed new lines do not belong to such frequencies. A determination of the heat capacities of the substance at very low temperatures, and comparative studies similar to one attempted in the following section may help to clear up the question.

§ B.

The heat capacities of carbon disulphide have been recently measured by Brown and Manov⁵ through a wide range of temperatures down to 15.05°K . It is now possible, therefore, to compare these values with heat capacities deduced from the frequencies of new Raman lines of the substance observed at low temperatures, by working along the lines indicated in a previous communication.

The molecule is known to be symmetrical triatomic linear, having the symmetry elements $D_{\infty h}$. Selection rule, therefore, forbids the appearance of lattice oscillations (in the solid state) of this centro-symmetrical molecule in Raman effect. The spectrum of the solid, however, shows the presence of two new lines at 70 and 80 cm^{-1} , of which the first is more intense than the totally symmetrical vibrational line at 655 cm^{-1} . It is therefore improbable that these lines might be due to lattice oscillations. The two lines might also be attributed to the two modes of angular oscillations postulated by Pauling⁶ (about the two axes perpendicular to the axis of the molecule), but from the identical character of these two vibrations, it follows that these should involve almost equal changes of molecular polarisability and should therefore be of approximately equal intensities. Experimental results show that the line at 70 cm^{-1} is about ten times as intense as that at 80 cm^{-1} .

Contributions to specific heat due to these frequencies have been calculated on two alternative assumptions, *viz.*, taking these as (a) lattice vibrations, the line 70 being twofold and the line 80 a single, and (b) Pauling angular oscillations. The results, some of which have been shown in the accompanying table, show no agreement with the observed heat capacities. On the other hand, when these

frequencies are regarded as being due to inter-molecular vibrations arising out of some electronic binding between pairs of molecules, their contributions, each $\frac{1}{2} R E(\theta/T)$, where E represents Einstein function, together with a Debye frequency (threefold) and a suitable Pauling frequency (twofold), which have not appeared as Raman lines, show satisfactory agreement with the observed values of heat capacities from the lowest temperature to just below the melting point. The differences between the observed values of C_p and the calculated values of C_p are easily attributed to the expected values of $C_p - C_v$, which gradually increases from zero at the lowest temperature to greater and greater values. The approximate relation $C_p - C_v = 0.014 (T/T_m) \times C_p^2$, T_m being the melting point, indicates that the differences between the experimental values of C_p and the calculated values of C_v are of the right order of magnitude. Also the contribution of the frequency 391.5 cm^{-1} due of the antisymmetric vibration of the CS_2 molecule becomes appreciable at temperatures a few degrees below the melting point and this accounts for the large difference between calculated values of C_v for these temperatures without taking into consideration the frequency 391.5 cm^{-1} , and the observed values of C_p .

(1)	(2)	(3)	(4)	(5)	(6)	(7)
T	$\frac{1}{2} R D(\theta_1/T)$ $+ \frac{1}{2} R D(\theta_2/T)$ $\theta_1 = 100^\circ.5$ $\theta_2 = 114^\circ.7$	$\frac{1}{2} R \sum E(\theta_i/T)$ 1	$\frac{3}{2} R D(\theta'/T)$ $\theta' = 91^\circ.0$	$2 R E(\theta''/T)$ $\theta'' = 206^\circ.9$	C_v calc. (3) + (4) + (5)	C_p obs.
15.05	1.16	.09	1.56	.00	1.65	1.65
20.15	2.05	.28	2.56	.01	2.85	2.87
26.19	2.99	.58	3.49	.09	4.16	4.18
29.76	3.43	.75	3.89	.18	4.82	4.56
37.67	4.16	1.05	4.52	.49	6.06	6.32
42.22	4.44	1.18	4.78	.72	6.68	6.92
52.25	4.91	1.41	5.14	1.23	7.78	7.91
63.47	5.21	1.57	5.39	1.75	8.71	8.92
75.54	5.38	1.68	5.54	2.20	9.42	9.57
87.21	5.54	1.75	5.59	2.53	9.87	10.31
99.00	5.63	1.81	5.71	2.79	10.31	10.98
108.93	5.66	1.83	5.73	2.97	10.55	11.59
119.01	5.73	1.86	5.70	3.11	10.76	12.07
131.54	5.77	1.88	5.81	3.25	10.94	12.58
144.31	5.8	1.90	5.84	3.35	11.09	13.05
155.63	5.82	1.91	5.86	3.43	11.20	13.50
158.71	5.83	1.91	5.86	3.45	11.22	14.46

It is easily seen from the table that the specific heat values calculated on the basis of the new Raman lines being treated as lattice frequency lines (column 2) show no agreement with the experimental values (column 7).

CONCLUSION.

A view, alternative to that in which the new lines were regarded as due to either lattice oscillations or Pauling angular vibrations, originally put forward by

Sirkar, has been already discussed in a previous communication,⁷ where it was pointed out how the assumption of a weak electronic type of binding between molecules helps to explain many apparently inexplicable facts about these new lines. The observations with tartaric acid and sodium tartrate crystals are also readily understood. Since ionic crystals can hardly form molecular aggregates, due to repulsion between similar ions, no evidence of the formations of polymers of sodium tartrate should be obtainable. The possibility of the formation of groups arises with molecular crystals, e.g., tartaric acid, benzophenone etc., due to their electro-neutrality, and the new lines observed with these might be due to unknown types of vibrations of such groups. It is evident also that contributions of such vibrations to specific heat would be derived from their corresponding Einstein functions and not from Debye.

It should be admitted that no sufficiently conclusive proof of the formation of groups in the solid state is yet obtainable. The binding energy being weak (because the frequencies are very low), it may never be possible to detect it from a shortening of the intermolecular distance by X-ray analysis. The difficulties in explaining the presence, and behaviour of these lines to changes of temperature etc., are however easily discernible from this and all previous communications. It is believed that specific heat calculations from these new frequencies will greatly help to understand their origin, and so a systematic calculation with other substances has been undertaken, after recording the new frequencies in the respective solids, whose specific heats have been determined accurately at low temperatures by other workers.

The author is indebted to Prof. M. N. Saha, Palit Professor of Physics, for providing all facilities of his laboratory, and to Sir P. C. Rây and Dr. S. C. Sirkar for their kind interests and guidance.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA

REFERENCES.

- ¹ Sirkar and Gupta, *Ind. J. Phys.*, **12**, 35 (1938).
- ² Sirkar, S. C., *Ind. J. Phys.*, **11**, 343 (1937).
- ³ Menzies and Mills, *Proc. Roy. Soc.*, **148A**, 407 (1935).
- ⁴ Bragg, *X-rays and Crystal Structure*.
- ⁵ Brown and Manov, *J. Am. Chem. Soc.*, **59**, 500 (1937).
- ⁶ Pauling, *Phys. Rev.*, **36**, 430 (1930).
- ⁷ Sirkar and Gupta, *loc. cit.*

STRATIFICATION OF THE IONOSPHERE AND THE ORIGIN OF THE E₁ LAYER*

By J. N. BHAR, M.Sc.,

Sir Rashbehary Ghose Research Scholar in Physics.

(Received for publication, October 21, 1938.)

ABSTRACT. Calculations of upper atmospheric ionisation are made after Pannekoek with certain modifications. It is assumed that the upper atmosphere above 100 km. consists mainly of N₂ and O while the lower and the middle atmosphere below this level consists of N₂ and O₂. There is a layer of transition between the two occupying the region 80-130 km. The temperature in the upper atmosphere is assumed to be 600°K. and that in the transition layer 300°K. The sun is taken to be radiating like a black body at 6800°K. Calculations show that there are ionisation maxima at 250 km. due to O, at 160 km. due to N₂ and 90 km. due to O₂. These three maxima are identified with the F₂, F₁ and E₁ regions.

The most interesting point to be noted is that attempts at obtaining from theoretical considerations a layer of ionisation at the height of the E₁ region have hitherto failed. This, in fact, prompted Chapman to put forward the hypothesis that the ionisation of the F region was due to ultra-violet radiation while that of the E region was due to the bombardment of neutral corpuscles shot off from the sun. It is well-known that observations during solar eclipses prove definitely that the E₁ region ionisation is also due to solar ultra-violet radiation. The work described here thus removes the anomaly regarding the formation of the E₁ layer. It can now be definitely asserted that the region round 100 km. in which rapid transition of O₂ to O occurs is also, as a consequence, the region of maximum ionisation of O₂ and that the ionised layer formed near this level is to be identified with the E₁ layer.

INTRODUCTION

The ionosphere is now known to be stratified into a number of regions or layers of maximum ionisation. The layers of most persistent ionisation are in the upper atmosphere above 90 km. In recent years strong evidence¹ has been obtained of the occurrence of ionised regions in the middle (15-90 km.) and also in the lower (0-15 km.) atmosphere. The heights and the accepted nomenclature of these regions of ionisation are given in the table below.

	Equivalent height.	Nomenclature.
Lower atmosphere	0-15 km.	C ₁ region
Middle atmosphere	15-45 "	C ₂ "
	50-5 "	D "
Upper atmosphere	90-120 "	E ₁ "
	150-170 "	F ₂
	180-220 "	F ₁
	220 km. upwards	F ₀

* Communicated by the Indian Physical Society.

Of the layers in the upper atmosphere E_1 and F_2 are permanent features of the ionosphere and are found to exist at all times of the day and night throughout the year. E_2 and F_1 are generally present during the daytime. Compared with the layers in the upper atmosphere, those in the middle and the lower atmosphere are very irregular in occurrence. In fact more recent observations² appear to show that the B and the C regions occur only occasionally as patches or blobs of ionisation which can reflect radio waves.

The origin of the stratification is still ill-understood though the agency causing the ionisation is now known more or less definitely to be the solar ultra-violet radiation. Besides the solar radiation a number of agencies of geophysical origin like thunderstorms, meteoric showers, etc., have also been suggested as producing ionisation, the former particularly in the lower regions of the ionosphere. Appleton³ suggested in 1933 that the four uppermost regions are connected with the ionisation potentials of nitrogen and oxygen atoms and molecules, though he did not offer any definite explanation as to the mechanism of the stratification.

Pannekoek⁴ in 1926 developed a method of computing upper atmosphere ionisation by assuming the sun as a black radiator and applying Woltjer's⁵ extension of Saha's theory of thermal ionisation. Since in this theory the absorption of the ionising radiation by each of the constituents is considered separately it is to be expected that the different constituents should, in general, yield different distributions of ionisation with height. The stratification and other details of the ionosphere were unknown at the time of Pannekoek's work and the significance of the results of his analysis were not properly appreciated when his paper was published.

After the discovery of the two main stratifications of the ionosphere, E_1 and F_2 , Chapman⁶ in 1931 attempted to apply Pannekoek's analysis to explain the stratification by assuming the upper atmosphere to consist of N_2 , O_2 and O and taking the temperature to be about 300°K. Chapman was unable to trace the origin of the ionisation maximum at the level of the E_1 region, i.e., at about 100 km., to any known process of atomic or molecular ionisation. This result, as is well-known, led him to offer the hypothesis that the upper layer is due to the action of solar ultra-violet radiation and the lower one to the action of high speed neutral corpuscles shot off from the sun. Subsequent observations during solar eclipses,⁷ however, failed to substantiate Chapman's theory. At the same time Chapman⁸ developed his theory of ionisation by considering the absorption of monochromatic radiation in an atmosphere rotating with the earth. The results of his analysis have been widely utilised for studying the variation of ionisation at different hours of the day and night and in different latitudes. It has recently been shown by Saha and Rai⁹ that Chapman's theory if it were 'properly developed and extended,' would have led to the same result as that of Pannekoek.

Since the publication of Chapman's work our ideas regarding the state and constituents of the upper atmosphere have undergone considerable modification. In view of this it is desirable that the problem of the stratification of the ionosphere be re-examined in the light of our newer knowledge regarding the upper atmosphere. This has been done recently by the writer both with regard to the formation of the upper F_1 and F_2 layers and the lower E_1 layer. A communication¹⁰ on the former was made to the Mathematics and Physics section of the Indian Science Congress (January, 1938) and the results arrived there are described here after revised calculations. In the present paper the question of the E_1 layer ionisation is also discussed. In connexion with this latter it should be mentioned that it had not been hitherto possible to explain the ionisation at the level of the E_1 layer by the application of Pannekoek's theory. In a recent paper by Hulburt¹¹ in which he has utilised Pannekoek's formula in a modified form, no indication of ionisation below 200 km. was obtained. It will be shown below that this curious result of the analyses by the above workers, namely, no evidence of ionisation at the E_1 layer level, may be traced to the special nature of the assumptions made regarding the distribution of O_2 . Hulburt has assumed that O_2 is distributed above 110 km. according to Dalton's law, the temperature of the atmosphere being $360^\circ K$. The distribution of O_2 assumed by Chapman has not been definitely mentioned. It is now believed, however, that due to the photo-dissociating effect of the solar radiation all the O_2 molecules above about 130 km. are completely dissociated to O . There is thus a layer of transition between, say, 80 km. and 130 km. in which O_2 is transformed to atomic oxygen. Consideration of the photo-ionisation of O_2 in this region of transition shows that an extremely thin ionised layer is formed with a maximum of ionisation at about 100 km. level. *The definite assertion can thus be made that the 100 km. level which is the level of rapid transition of O_2 to O is also, as a consequence, the level of maximum ionisation of O_2 and the ionised layer formed in this region is to be identified with the E_1 layer.*

2. PANNEKOEK'S METHOD AND ITS MODIFICATION

As mentioned above Pannekoek's method of treating the ionisation of the upper atmosphere has been the earliest and is the most general method. In our calculations of the distribution of ionisation due to the various gases, we will use Pannekoek's method* with certain minor modifications. We now proceed to discuss briefly the derivation of the working formula which we have actually employed in section 5.

* I am greatly indebted to Prof M. N. Saha for the kind help I received from him in clearing up a number of points in Pannekoek's theory and also for helpful criticisms regarding the contents of this paper. Fig. 1 depicting the absorptions by N_2 and by O_2 in the region $\lambda < 1000\text{\AA}$ is drawn at his suggestion.

(a) *Woltjer and Milne's extension of the Saha Ionisation Formula*

The theory of the ionisation of elements by the heat was, as is well-known, first given by Saha¹² in 1921. The fraction of a hot gas which is ionised is given by

$$\frac{y^2}{1-y^2} \cdot p = \frac{(2\pi m_e)^{3/2}}{h^3} (kT)^{5/2} e^{-\chi/kT} \quad \dots (1)$$

where y is the fraction of the gas ionised,

p —the total pressure due to the ions, electrons and neutral atoms (dynes/cm²),

m_e —the mass of electrons (gms.),

T —the absolute temperature of the gas in the equilibrium state (degrees absolute),

h —Planck's constant,

k —Boltzmann's constant,

χ —energy of ionisation per atom (ergs).

The formula strictly holds when the gas, the electrons, the ions and the radiation are in perfect thermodynamical equilibrium. One however meets with difficulty if one tries to apply the formula to the case of the atmosphere of a star, say, that of the sun, which is at a temperature of about 500°K but which is traversed by radiation at a temperature as high as 6800°K emanating from the photosphere. The case might be compared to the laboratory experiments in which light from an arc at 4000°C emitting like a black body is made to traverse a column of sodium vapour at a temperature of 400° to 500°C. Since the case of ionisation of the earth's atmosphere belongs to this class—the temperature of the atmospheric gases being, say, 300° to 1500°K while the temperature of solar radiation is 6800°K—the Saha ionisation formula as given above in its original form cannot be applied. One has therefore to suitably modify the ionisation formula in order to apply it to the case under discussion.

A preliminary attempt in this direction was made by Saha and Sur¹³ but the correct formula was later derived by Woltjer. The thermodynamical derivation of this formula is rather complicated. An easier deduction based on kinetic theory considerations was given by Milne¹⁴ in 1924. Starting from this formula we shall proceed to compute the ionisation of the upper atmosphere according to the method indicated by Pannekoek introducing the necessary modifications at their proper places.

Woltjer showed that

$$\frac{n_i n_e}{N} = \left[\frac{n_i n_e}{N} \right]_0 \frac{\int_{\nu_0}^{\infty} \psi_{\nu} I_{\nu} d\nu}{\int_{\nu_0}^{\infty} \psi_{\nu} e^{-h\nu/kT} \left(I_{\nu} + \frac{8\pi h \nu^3}{c^2} \right) d\nu} \quad (2)$$

where n_i is the number of ions per unit volume,

n_e —number of electrons per unit volume,

N —number of atoms per unit volume,

ν —frequency of the radiation,

I_{ν} —intensity of the radiation of frequency ν ,

ψ_{ν} —probability coefficient, it gives the fraction of the total number of atoms ionised when radiation of unit intensity and of frequency ν is incident upon them,

$\left[\frac{n_i n_e}{N} \right]_0$ —value of $\frac{n_i n_e}{N}$ in the equilibrium condition, i.e., when radiation is at the same temperature with the gas,

ν_0 —threshold frequency for ionisation,

T —temperature of the gas in degrees absolute,

c —velocity of light.

(b) *Modification of the above Formula for Limited Range of Integration over which Photo-electric Absorption is assumed Constant*

The evaluation of the integrals involved in eqn (2) requires a knowledge of ψ_{ν} as a function of ν . Pannekoek has assumed ψ_{ν} to be proportional to ν^{-3} . It is known, however, that ψ_{ν} is connected with the atomic absorption coefficient γ_{ν} by the relation

$$\psi_{\nu} = \gamma_{\nu} / h\nu.$$

As will be seen later on we shall assume the absorption coefficient to be constant over a limited range of integration. It follows from this assumption that $\psi_{\nu} = A/\nu$ (where A is a constant) within these limits.

We may therefore write eqn. (2) as

$$\frac{n_i n_e}{N} = \left[\frac{n_i n_e}{N} \right]_0 \frac{\int_{\nu_0}^{\nu'} I_\nu / \nu \cdot d\nu}{\int_{\nu_0}^{\nu'} \frac{1}{\nu} \cdot e^{-h\nu/kT} \left(I_\nu + \frac{8\pi h\nu^3}{c^2} \right) d\nu}$$

where ν_0 and ν' are the limits between which the photo-electric absorption coefficient γ_ν is assumed to be constant.

Since, $e^{h\nu/kT_1} \gg 1$, we may put

$$I_\nu = \frac{8\pi h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT_1}}$$

$$\ll \frac{8\pi h\nu^3}{c^2}, \text{ where } T_1 \text{ is the temperature of the black body.}$$

Remembering these, the above eqn. becomes

$$\begin{aligned} \frac{n_i n_e}{N} &= \left[\frac{n_i n_e}{N} \right]_0 \frac{\int_{\nu_0}^{\nu'} \frac{8\pi h\nu^2}{c^2} \cdot e^{-h\nu/kT_1} d\nu}{\int_{\nu_0}^{\nu'} \frac{8\pi h\nu^2}{c^2} \cdot e^{-h\nu/kT} d\nu} \\ &= \left[\frac{n_i n_e}{N} \right]_0 \frac{\int_{x_{10}}^{x_1'} x_1^2 e^{-x_1} dx_1}{\int_{x_{10}}^{x_1'} x_1^2 e^{-x_1} dx_1} \end{aligned}$$

where $x_1 = h\nu/kT_1$ and $x = h\nu/kT$.

Now it can be proved that

$$\frac{n_i n_e}{N} = \frac{y^2}{1-y^2} \cdot \frac{p}{kT},$$

y having its previous significance.

Taking this into account and substituting the value of $\left[\frac{n_i n_e}{N} \right]_0$ from the original Saha formula (eqn. 1), we get

$$\frac{y^2}{1-y^2} p = \frac{(2\pi m_e)^{\frac{5}{2}}}{h^3} \cdot k^{\frac{5}{2}} \cdot T^{\frac{3}{2}} T^{-\frac{1}{2}} e^{-\chi/kT} \frac{\int_{x_{10}}^{x'} x_1^2 e^{-x_1} dx_1}{\int_{x_0}^{x'} x^2 e^{-x} dx} \quad \dots (3)$$

where p is in dynes/cm.² and χ is in ergs

The expression on the right hand side of this equation is different from that of Pannekoek. If, however, the values of the limits x_0 and x' are such that

$$\int_{x_0}^{\infty} x^2 e^{-x} dx \gg \int_{x'}^{\infty} x'^2 e^{-x'} dx'$$

and that $x^2 \gg x$

then it is easy to show that eqn. (3) takes the form

$$\frac{y^2}{1-y^2} \cdot p = \frac{(2\pi m_e)^{\frac{5}{2}}}{h^3} \cdot k^{\frac{5}{2}} T_1^{\frac{3}{2}} T^{-\frac{1}{2}} e^{-\chi/kT_1} \quad \dots (4)$$

which is the same as that of Pannekoek's.

3. APPLICATION TO THE EARTH'S ATMOSPHERE .

In calculating upper atmospheric ionisation from eqn. (3) it is necessary, first of all, to find out what fraction of the total energy radiated by the sun per second enters into the earth's atmosphere. The value of this fraction is $\omega/4\pi = \beta$, say, where ω is the solid angle subtended by the sun at the earth. Chapman⁶ and Saha and Rai⁹ have taken $\beta = 1/230,000$; we shall also use this value. Hence we have to multiply the right hand side of eqn. (3) by β so that we get

$$\frac{y^2}{1-y^2} \cdot p = \beta \frac{(2\pi m_e)^{\frac{5}{2}}}{h^3} \cdot k^{\frac{5}{2}} T_1^{\frac{3}{2}} T^{-\frac{1}{2}} e^{-\chi/kT} \frac{\int_{x_{10}}^{x'} x_1^2 e^{-x_1} dx_1}{\int_{x_0}^{x'} x^2 e^{-x} dx} = K, \text{ say} \dots (5)$$

Now the density of ionisation at any point due to the photo-ionisation of a particular gas depends upon the intensity of the effective radiation reaching that point. This intensity will, in its turn, depend upon the absorption suffered by the radiation in passing through the superincumbent atmosphere. This latter can be calculated if we know the coefficient of absorption γ of the gas per atom or molecule and also the distribution of the pressure of the gas with height in the atmosphere.

We may therefore write eqn. (2) as

$$\frac{n_i n_e}{N} = \left[\frac{n_i n_e}{N} \right]_0 \frac{\int_{\nu_0}^{\nu'} I_{\nu} / \nu \cdot d\nu}{\int_{\nu_0}^{\nu'} \frac{I_{\nu}}{\nu} \cdot e^{-h\nu/kT} \left(I_{\nu} + \frac{8\pi h\nu^3}{c^2} \right) d\nu}$$

where ν_0 and ν' are the limits between which the photo-electric absorption coefficient γ_{ν} is assumed to be constant.

Since, $e^{h\nu/kT_1} \gg 1$, we may put

$$I_{\nu} = \frac{8\pi h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT_1}}$$

$$\ll \frac{8\pi h\nu^3}{c^2}, \text{ where } T_1 \text{ is the temperature of the black body.}$$

Remembering these, the above eqn. becomes

$$\begin{aligned} \frac{n_i n_e}{N} &= \left[\frac{n_i n_e}{N} \right]_0 \frac{\int_{\nu_0}^{\nu'} \frac{8\pi h\nu^2}{c^2} \cdot e^{-h\nu/kT_1} d\nu}{\int_{\nu_0}^{\nu'} \frac{8\pi h\nu^2}{c^2} \cdot e^{-h\nu/kT} d\nu} \\ &= \left[\frac{n_i n_e}{N} \right]_0 T_1^3 \cdot T^{-3} \frac{\int_{x_1 0}^{x_1'} x_1^2 e^{-x_1} dx_1}{\int_{x_0}^{x_0'} x^2 e^{-x} dx} \end{aligned}$$

where

$$x_1 = h\nu/kT_1 \text{ and } x = h\nu/kT.$$

Now it can be proved that

$$\frac{n_i n_e}{N} = \frac{y^2}{1-y^2} \cdot \frac{p}{kT},$$

y having its previous significance.

Taking this into account and substituting the value of $\left[\frac{n_i n_e}{N} \right]_0$ from the original Saha formula (eqn. 1), we get

$$\frac{y^2}{1-y^2} p = \frac{(2\pi m_e)^{\frac{3}{2}}}{h^3} \cdot k^{\frac{5}{2}} \cdot T^3 T^{-\frac{1}{2}} e^{-\chi/kT} \frac{\int_{x_{10}}^{x'} x_1^2 e^{-x_1} dx_1}{\int_{x_0}^{x'} x^2 e^{-x} dx} \quad \dots (3)$$

where p is in dynes/cm.² and χ is in ergs.

The expression on the right hand side of this equation is different from that of Pannekoek. If, however, the values of the limits x_0 and x' are such that

$$\int_{x_0}^{\infty} x^2 e^{-x} dx \gg \int_{x'}^{\infty} x'^2 e^{-x'} dx'$$

and that $x^2 \gg x$

then it is easy to show that eqn. (3) takes the form

$$\frac{y^2}{1-y^2} \cdot p = \frac{(2\pi m_e)^{\frac{3}{2}}}{h^3} \cdot k^{\frac{5}{2}} T_1 \cdot T^{\frac{3}{2}} e^{-\chi/kT_1} \quad \dots (4)$$

which is the same as that of Pannekoek's.

3. APPLICATION TO THE EARTH'S ATMOSPHERE

In calculating upper atmospheric ionisation from eqn. (3) it is necessary, first of all, to find out what fraction of the total energy radiated by the sun per second enters into the earth's atmosphere. The value of this fraction is $\omega/4\pi = \beta$, say, where ω is the solid angle subtended by the sun at the earth. Chapman⁶ and Saha and Rai⁹ have taken $\beta = 1/230,000$; we shall also use this value. Hence we have to multiply the right hand side of eqn. (3) by β so that we get

$$\frac{y^2}{1-y^2} \cdot p = \beta \frac{(2\pi m_e)^{\frac{3}{2}}}{h^3} \cdot k^{\frac{5}{2}} T_1^{\frac{3}{2}} T^{-\frac{1}{2}} e^{-\chi'/kT} \frac{\int_{x_{10}}^{x'} x_1^2 e^{-x_1} dx_1}{\int_{x_0}^{x'} x^2 e^{-x} dx} = K, \text{ say} \dots (5)$$

Now the density of ionisation at any point due to the photo-ionisation of a particular gas depends upon the intensity of the effective radiation reaching that point. This intensity will, in its turn, depend upon the absorption suffered by the radiation in passing through the superincumbent atmosphere. This latter can be calculated if we know the coefficient of absorption γ of the gas per atom or molecule and also the distribution of the pressure of the gas with height in the atmosphere.

Let us suppose that the density N_z of a gas at a height z above a certain datum level be given by

$$N_z = f(N_0, z) \quad \dots (6)$$

where N_0 is the number of molecules or atoms per c.c. at the datum level.

Let us now consider an atmospheric layer of thickness dz at the height z and of unit cross-section. The absorption of the radiation in passing through this layer will obviously be given by

$$\frac{dI}{I} = \gamma N_z dz$$

where I is the intensity at incidence,
 γ —the absorption coefficient per molecule or atom,
 and z is reckoned positive upwards.

Substituting for N_z from eqn. (6), we get

$$\frac{dI}{I} = \gamma f(N_0, z) dz$$

Integration yields

$$I = I_0 e^{\gamma \int_0^z f(N_0, z) dz} \quad \dots (7)$$

where I_0 is the intensity at the level at which N is zero, i.e., outside the atmosphere of the absorbing gas.

The distribution of pressure generally follows the exponential law, i.e.,

$$\begin{aligned} N_z &= f(N_0, z) \\ &= N_0 e^{-\theta z} \end{aligned}$$

where θ is a constant which determines the nature of the distribution. We then have

$$I = I_0 e^{-\gamma N_z / \theta}$$

It is evident, therefore, that to obtain the actual ionisation density produced by the incident radiation at the height z at which the density of the gas molecules or atoms is N_z the expression for K (eqn. 5) will have to be multiplied by the factor

$$e^{-\gamma N_z / \theta}$$

Thus

$$\frac{\gamma^2}{1 - \gamma^2} \cdot p = K e^{-\gamma N_z / \theta} \quad \dots (8)$$

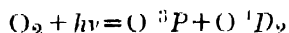
4. UPPER ATMOSPHERIC CONSTITUENTS, AND THEIR TEMPERATURE AND ABSORPTION COEFFICIENTS ASSUMED FOR THE CALCULATIONS

In order to evaluate the right hand side of eqn. (8) it is necessary that we know the properties of the atmosphere we are considering. A knowledge of the temperature, constituents and pressure distribution in the upper atmosphere as well as the absorption coefficients and the limits of absorption of the constituents is necessary. We give below the assumptions we have made with regard to these and also our reasons for making the same.

(a) *Upper Atmospheric Constituents and Temperature*

As mentioned in the introduction our ideas regarding the temperature and the constituents of the upper atmosphere have in recent years undergone considerable modification. Leaving aside the older view prevalent before the identification of the auroral green line (of atomic oxygen) that the higher regions of the atmosphere consisted of the hypothetical element geocoronium, the belief that the main constituents of the upper atmosphere were hydrogen and helium persisted for a very long time. These gases were subsequently shown to be liable to escape from the atmosphere owing to insufficient pull of gravity. The view held till recently had therefore been that the upper atmosphere constituents were N_2 and O_2 . Even this view is now losing ground and our latest conception regarding the upper atmosphere is that it consists of N_2 and O. The absence of O_2 is explained as due to the photo-dissociating action of the solar rays converting all the O_2 to O down to about 100 km. level. Since our calculations on the ionisation in the atmosphere will be based on the assumptions that the atmosphere below 100 km. consists mainly of N_2 and O_2 , and that above, of N_2 and O and there is a layer of transition between the two round about 100 km. we would discuss these points in a little more detail.

The dissociation of O_2 to O is brought about by the absorption of the continuum of the Runge-Schumann bands beyond λ_{1750A} according to the following reaction



The first atom is in the normal state and the second one in an excited state. Now since the process of recombination depends upon the pressure, the oxygen atoms in the rare high atmosphere will be almost permanently free while those in the lower and the comparatively denser atmosphere will recombine and produce O_2 . There will thus be a transition layer between the high and the middle atmosphere in which the amount of O_2 would rapidly increase with decreasing height while that of O would rapidly diminish till it is practically non-existent. Calculations carried

out recently by Majumdar,¹⁵ though not quite rigorous, show that the transition occurs fairly sharply and that the atmosphere at and above about 130 km. is almost entirely devoid of O₂.

On the basis of the above we have assumed the following constitution of the atmosphere. From the ground level up to 80 km. the atmospheric constituents are principally N₂ and O₂ (except of course the ozonosphere between 20 and 45 km.) in a more or less mixed state. Between 80 and 130 km. the density of the O₂ molecules decreases rapidly while that of O increases. This decrease of the density of O₂ we assume to occur exponentially according to the equation

$$N_z = N_0 e^{-\theta z}$$

where z is the height reckoned from the 80 km. level, N_0 the density at this level and θ is a constant. The value of N_0 is known to a fair degree of approximation from radio and other meteorological observations and is taken as equal to 1.6×10^{14} O₂-molecules/c.c.¹⁶ At 130 km. the number of O₂-molecules is greatly diminished, which we assume to be by a factor 0.625×10^{-10} , so that, it is 10^4 molecules/c.c. These assumptions give the value of θ to be 0.46×10^{-5} .

Above 130 km. we assume that the only gases present are N₂ and O and that these are in diffusive equilibrium under the action of gravity. In other words each of these constituents are distributed according to Dalton's law

$$N_z = N_0 e^{-mgz/kT} \text{ molecules/c.c.}$$

where N_0 is the density at the datum level (130 km.) in molecules/c.c.,
 m —the mass of each molecule,
 z —the height reckoned from the datum level,
 and T —the atmospheric temperature at the levels concerned.

It should be noted that we have assumed above that the upper atmosphere consists mainly of N₂ and O. In other words, we have assumed that unlike O₂, N₂ is not photo-dissociated. This assumption is based on the fact that the forbidden lines of N are apparently absent in the light of the night sky and of the aurorae. According to Saha,¹⁷ however, this apparent absence is not to be regarded as a criterion for the absence of N in the upper atmosphere. To quote his remarks,—

“ The forbidden lines of nitrogen are

${}^4S - {}^2D = \nu$	$\left. \begin{array}{l} 19223 \\ 19231 \end{array} \right\}$	$\begin{array}{l} 5202.1 \\ \lambda \\ 5199.9 \end{array}$
${}^4S - {}^2P = \nu$	$\left. \begin{array}{l} 28840 \\ 9617 \end{array} \right\}$	$\begin{array}{l} \lambda 3467.4 \\ 10398.3 \\ \lambda \\ 10410.2 \end{array}$
${}^2D - {}^2P = \nu$	$\left. \begin{array}{l} 9617 \\ 9606 \end{array} \right\}$	

The last is in the infra-red and has not yet been observed either in the morning or the evening flash. $^4S-^2P$, $\lambda 3467\cdot4$, is too far in the ultra-violet and has not yet been found. $^4S-^2D$, $\lambda 5202$, is promising, but it is unfortunately mixed up with the (0,2) bands of N_2 . Sommer at one time identified the line observed near $\lambda 5206$ as being the $^4S-^2D$ line of N, but the matter needs careful reinvestigation. The discussion shows that as yet there is no definite evidence for the presence of forbidden lines of N in the night-sky spectrum, but this does not absolutely exclude the possibility of their occurrence."

Since the above was written by Saha, Kaplan⁸ and also Bernard¹⁹ simultaneously reported the existence of a line $\lambda 3470$ in the spectra of the light of the night sky and of aurorae. This has been provisionally identified with the line $^4S-^2P$, the wave-length of which is $\lambda 3467\cdot4\text{\AA}$. In a private letter to Prof. Saha, Prof. Kaplan informs him that his new measurement with an apparatus of higher dispersion gives the wave-length as $\lambda 3467\text{\AA}$. It seems, therefore, that the identification is satisfactory and that one cannot altogether deny the existence of atomic nitrogen in the upper atmosphere. However, in the absence of more detailed knowledge regarding the presence and distribution of atomic nitrogen we have in the present communication thought fit to omit the consideration of this gas in subsequent discussions.

It may also be noted here that the hypothesis that the upper atmosphere consists chiefly of N_2 and O raises a difficulty with regard to the explanation of the production of aurorae at great heights—1000 km. and above. The spectra of the aurorae give unmistakable evidence of the presence of molecular nitrogen but it is difficult to see how N_2 molecules can reach such great heights. On account of diffusive separation between N_2 and O, the former will occupy the comparatively lower regions of the upper atmosphere and the highest regions will consist mainly of atomic oxygen. This difficulty, which is a serious one and to which attention has been drawn by several workers, can be met with if we accept the auroral hypothesis developed recently by Hulburt and Maris.²⁰ According to these authors nitrogen molecules producing the aurorae do not attain the auroral heights from the denser atmosphere directly below the aurorae but are transported to the auroral regions from the lower atmosphere above the equatorial regions by being ionised by the solar rays and guided by the terrestrial magnetic field.

The temperature of the high atmosphere which we are concerned with is still a matter of speculation. Anomalous variations in the electron density of the F region of the ionosphere lend support to the hypothesis of a high temperature in this region. Martyn and Pulley¹⁶ think that the temperature between 100 km. and 300 km. level rises linearly from 300° to 1200°K . In view of the still doubtful nature of this too definite assumption we have taken the temperature to be uniform and 600°K . The temperature between 80 and 130 km. in the transition layer ($O_2 \rightarrow O + O$) is taken to be 300°K . Consideration in regard to the application of Pannekoek's method for calculating the ionisation

distribution is also one of the reasons for assuming a constant temperature. In the case of the temperature varying with height, as Wildt²¹ has shown, the theory of thermodynamical equilibrium no longer holds.

In table I the assumptions regarding the composition, pressure distribution and temperature described above are summarised.

TABLE I.

Region.	Mean Temp. T.	Constituents.	Density Distribution.
80 km. to 130 km.	300° K	O ₂ , N ₂ , and O	For O ₂ $N_z = N_0 e^{-\theta z}$ $N_0 = 1.6 \times 10^{14}$ molecules/c.c. $\theta = 4.6 \times 10^{-6}$ Datum level—80 km.
130 km. upwards	600° K	O and N ₂	$N_z = N_0 e^{-mgz/kT}$ $N_0 \begin{cases} = 4 \times 10^{11} \text{ atoms/c.c. for O} \\ = 1.6 \times 10^{12} \text{ molecules/c.c. for N}_2 \end{cases}$ Datum level—130 km.

The values of N_0 for N_2 and O at 130 km. are calculated from the data given in a recent paper by Mitra and Rakshit²² on the distribution of the constituent gases in the upper atmosphere.

(b) The Coefficients of Absorption

In section 3 we have seen how the ionisation formula (eqn. 2) should be modified when one is to calculate the ionisation of a gas of which the absorption coefficient is constant within certain frequency limits. Our knowledge regarding the absorption coefficients of the constituents which we are considering are extremely meagre. All previous workers on this problem have utilised the well-known formula of Kramers²³ developed for X-ray absorption :

$$\gamma_\nu = \frac{16\pi^2}{3\sqrt{3}} \cdot \frac{Z^2 e^6}{c} \cdot \frac{\nu_0}{(h\nu)^3}$$

We will also do the same* for O_2 and N_2 . For atomic oxygen we will utilise the value of the absorption coefficient recently obtained by Saha and Rai⁹ from wave mechanical considerations.

It will be seen that Kramers' formula involves the atomic number Z . When applied to the case of molecules like N_2 and O_2 , Z cannot obviously be identified with the ordinary atomic number on account of the effect of "screening" of the nuclear charge due to the presence of the outer electrons. To compensate for the screening effect the calculated value of γ_{v_0} (for $v=v_0$) has to be multiplied by a fraction. The magnitude of this fraction can be estimated by comparing the value of the absorption coefficient for O as deduced from Kramers' formula with that deduced quantum mechanically by Saha and Rai. This fraction is found to be (Saha and Rai : Kramers) $1/9$ for the process $O^3P \rightarrow O^1S$. It will not be unreasonable to assume that the fraction is of the same order for O_2 and N_2 . On account, however, of the uncertainty and also the large range of values possible we have carried out our calculations by assuming this fraction to be $1/10$ and $1/50$, so that if at any future date more exact values of the absorption coefficient be available either experimentally or from theoretical considerations it may be possible to identify the results of one or other of the above sets of calculations as the actual ionisation distribution.

(c) Limits of Absorption

The limits of the wave-length ranges absorbed by the gases with which we are concerned may be obtained from spectroscopic data. Our knowledge regarding the absorption of ultra-violet light by N_2 , O_2 and O has been collected by Saha,^{17, 26} and by Chapman and Price.²⁷ For convenience, we present here the collected data only for wave-lengths $\lambda < 1000\text{\AA}$, in the accompanying table, since it appears that wave-lengths above this value cannot appreciably ionise any of the above atmospheric gases.†

* The applicability of Kramers' law to the cases in question is open to serious objection,⁹ though till recently it was being used by various authors in connection with astrophysical problems. Recently T. L. Page²⁴ of Oxford has carried out experiments to test the validity of this law in the case of the hydrogen atom and has concluded from his results that the use of Kramers' law in astrophysical problems is unjustified. A very interesting discussion in this connection in which several eminent astrophysicists took part has been recently published in "The Observatory."²⁵

† There is a possibility that atoms or molecules in some of the excited states may be photo-ionised by light of frequency less than that corresponding to the observed ionisation potentials. But this possibility is left out of consideration in the present discussion.

TABLE 2.

	Spectral Region.	Phenomena observed.	Remarks.
Molecular Nitrogen	$\lambda\lambda 1000-795\text{\AA}$	Rydberg sequence of absorption bands converging to the limit $\lambda 795\text{\AA}$. A few tenths of a mm. at N.T.P. cause almost complete absorption.	First observed by Price and recently by Worley and Jenkins. ²⁸
	$\lambda < 795\text{\AA}$	Continuous absorption commencing at $\lambda 795\text{\AA}$ (15.573 e.v.). Each quantum absorbed produces N_2^+ normal and electron. A few tenths of a mm. at N.T.P. show the continuum.	Observed by Worley and Jenkins. ²⁸
	$\lambda\lambda 795-661\text{\AA}$	Rydberg sequence of absorption bands converging to the limit $\lambda 661\text{\AA}$. A few hundredths of a mm. at N.T.P. suffice to bring out the absorption spectra.	Observed by Hopfield ²⁹ and recently by Takamine and others. ³⁰
	$\lambda < 661\text{\AA}$	Continuous absorption commencing at $\lambda 661\text{\AA}$ (18.67 e.v.). Each quantum absorbed produces N^+ excited and electron. Absorption same as above	"
Molecular Oxygen	$\lambda\lambda 1300-1019\text{\AA}$	Series of diffuse absorption bands tending to the limit $\lambda 1019\text{\AA}$. A few tenths of a mm. at N.T.P. produce complete absorption	Observed by Price and Collins. ³¹
	$\lambda < 1019\text{\AA}$	An expected continuum of absorption commencing at $\lambda 1019\text{\AA}$ (12.2 e.v.). Each quantum absorbed should produce O_2^+ normal and electron. Very weak absorption.	Not yet definitely observed
	$\lambda\lambda 1000-670\text{\AA}$	(i) Complicated system of absorption bands (H, I, ...) which may be fitted into a Rydberg sequence converging to the limit $\lambda 764.7\text{\AA}$ (16.14 e.v.). (ii) Another system of bands (M, N, ...) forming Rydberg sequence converging to the limit $\lambda 744\text{\AA}$ (16.5 e.v.). (iii) A third system of bands (P, Q, ...) forming Rydberg sequence passing to the limit $\lambda 670\text{\AA}$ (18.25 e.v.) (iv) An ionisation continuum corresponding to the second system (M, N, ...) of bands starting abruptly at about $\lambda 740\text{\AA}$ (16.7 e.v.). Absorption in all the above cases is very strong, a few hundredths of a mm. at N.T.P. being sufficient to show the bands clearly.	Observed by Hopfield and by Price and Collins. ³¹

TABLE 2 (contd.).

	Spectral Region.	Phenomena observed.	Remarks.
Atomic Oxygen	$\lambda < 920\text{\AA}$	Each quantum absorbed leads to the reaction : $\text{O}^3P \rightarrow \text{O}^1S$ (13.55 e.v.)	The intensity of absorption is not known experimentally. Absorption coefficient calculated theoretically by Saha and Rai is 2.18×10^{-17} cm. ² per atom.
	$\lambda < 858\text{\AA}$	$\text{O}^1S \rightarrow \text{O}^3P$ (14.4 e.v.)	Effect negligible
	$\lambda < 744$	$\text{O}^1D \rightarrow \text{O}^3P$ (16.5 e.v.)	"

In fig. 1 the data collected in the above table are represented graphically.

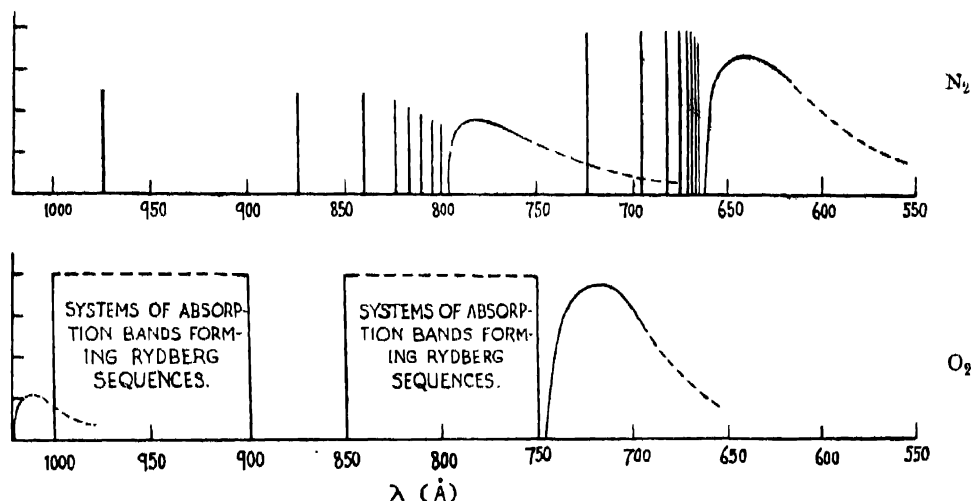


Fig. 1 -- Absorption spectra of N_2 and O_2 . The vertical lines represent the positions of the observed absorption bands while the heights of these lines represent the relative intensities of absorption approximately.

The ionisation of any of the constituent gases may, from considerations of the data given above, be regarded as the result of absorption of light within a particular range of wave-lengths, e.g., $\lambda 910\text{--}744\text{\AA}$ for atomic oxygen, $\lambda 744\text{--}661\text{\AA}$ for molecular oxygen and $\lambda < 661\text{\AA}$ for molecular nitrogen. The lower wave-length limit of absorption of nitrogen is not known but for purposes of calculation we shall take it as $\lambda 585\text{\AA}$.

In table 3, the limits of the absorption ranges, the coefficients of absorption γ_{ν_0} and the ionisation potentials of N_2 , O_2 and O arrived at in the light of the above considerations and used in our calculations are summarised.

TABLE

	Limit of absorption	Logarithm of coefficient of absorption.	Ionisation potential.
O	$\lambda\lambda 910\text{--}744\text{\AA}$ $\nu\nu 3\cdot314\ 4\ 036 \times 10^{15}$	$\overline{17}\cdot4487$	13.55 (e. v.)
O ₂	$\lambda\lambda 744\text{--}661\text{\AA}$ $\nu\nu 4\cdot036\text{--}4\cdot568 \times 10^{15}$	(i) $\overline{17}\cdot2344$ (ii) $\overline{18}\cdot5354$	16.5 (e. v.)
N ₂	$\lambda\lambda 661\text{--}585\text{\AA}$ $\nu\nu 4\cdot568\cdot5\cdot128 \times 10^{15}$	(i) $\overline{18}\cdot9852$ (ii) $\overline{18}\cdot2862$	18.67 (e. v.)

In the actual calculations it is necessary that we take into account the variation of γ_ν with frequency. In the case of O₂ and N₂, this variation follows, according to our assumption, Kramers' law, i.e., γ_ν varies as $1/\nu^3$. In the case of O, according to Saha and Rai,⁹ γ_ν varies as $\left(\frac{4}{\nu^3} - \frac{1}{\nu^4} \right)$. If these varia-

tions are taken into account over the ranges we are dealing with it is found (see Appendix) that the mean value of γ is of the order of $0.8\gamma_{\nu_0}$. Our calculations have been made with these mean values of the absorption coefficients, treating them as constants throughout the entire ranges of integration.

5. RESULTS OF CALCULATIONS

The values of K for O, O₂ and N₂ are calculated from eqn. (3) with the proper limits of the integrals given in table 3. It should be noted that for the particular values of the limits dealt with, eqn. (3) approximates, as pointed out in section 2 (b), very closely to Pannekoek's equation.

(a) Ionisation due to O

It may be seen in table 2 that the radiation in the range $\lambda\lambda 910\text{--}744\text{\AA}$ which is responsible for the photo-ionisation of O may also be partly absorbed by N₂. This latter absorption will evidently reduce the intensity of the radiation available for the ionisation of O and hence the ionisation density due to O will be less than what it would have been in the absence of N₂. The reduction, however, will not be very great since the relative density of the N₂ molecules at the heights at which the ionisation of O is produced is much smaller than that of O atoms. Lacking definite knowledge of the intensity of absorption by N₂ in this particular band, we shall assume that the radiation in this band is reduced to 0.05 of its original

value on this account. Hence, to calculate the ionisation due to O, we have to multiply the right hand side of eqn. (8) by the factor 0.05. Thus we have

$$1 - y^2 - p = 0.05 K e^{-\gamma N_z / \theta}$$

Remembering that n_e , the number of electrons or ions* per c. c., is given by $N_z y$, that $y^2 \ll 1$ and that $p = N_z kT$ we get

$$n_e = \sqrt{0.05 \frac{KN_z}{kT}} \cdot e^{-\frac{1}{2} \gamma N_z / \theta}$$

We have already assumed (Table 1) that the distribution of either of the gases N_2 and O obeys Dalton's law above 130 km. level. Hence the value of θ is mg/kT , where m is the mass of the oxygen atom.

The above equation gives the ionisation density corresponding to O at the height z at which the number of atoms per c. c. is N_z .

(b) Ionisation due to O_2

The wave-length range responsible for the ionisation of O_2 is $\lambda\lambda 744\text{--}661\text{\AA}$. There is, however, absorption by N_2 and O near this range of wave-lengths commencing from $\lambda 800\text{\AA}$ and from $\lambda 744\text{\AA}$, respectively. We have assumed that O_2 exists in the lower and in the middle atmosphere and also that there is a transition layer in which O_2 is gradually replaced by O between 80 and 130 km. The ionising wave-lengths (for O_2) $\lambda\lambda 744\text{--}661\text{\AA}$ will, therefore, be partly absorbed by the overlying N_2 and O before reaching the transition layer. The value of the absorption coefficient of O is not known. Our only knowledge regarding the absorption by N_2 is that a few hundredths of a mm. of nitrogen at N.T.P. suffice to show the bands commencing at $\lambda 800\text{\AA}$. The amount of N_2 and O above 130 km. being about 0.9 and 0.45 mm. at N. T. P., it would not be very wide of the mark if we assume that the intensity of the ionising radiation reaching the transition layer is reduced by a factor 0.001. This reduced value of the intensity of the incident radiation is used in our calculations. We thus have

$$\frac{y^2}{1 - y^2} - p = 0.001 K e^{-\gamma N_z / \theta}$$

And as before

$$n_e = \sqrt{0.001 \frac{KN_z}{kT}} \cdot e^{-\frac{1}{2} \gamma N_z / \theta}$$

where

$$\theta = 1.6 \times 10^{-6} \text{ (see table 1).}$$

* We are dealing with unicomponent systems, so that $n^+ = n_e$.

(c) Ionisation due to N₂

Radiation of wave-lengths in the range $\lambda\lambda < 661\text{\AA}$ which can ionise N₂ is not known to be absorbed by any of the above gases. In this case, therefore, we have simply

$$n_e = \sqrt{\frac{K N_2}{kT}} e^{-\frac{1}{2}\gamma N_2 / \theta}.$$

where $\theta = mg/kT$, m being the mass of the N₂ molecule.

We now tabulate the values of K , γ , T and θ for the respective constituents.

TABLE 4.

	O	O ₂	N ₂
log ₁₀ K	8.616	11.4	12.2316
log ₁₀ γ	17.3348	(i) 17.1597	(i) 18.9053
		(ii) 18.4607	(ii) 18.2063
T	600°K	300°K	600°K
log ₁₀ θ	7.5010	6.6628	7.7441

With the help of the above data, the values of n_e for different values of N_2 are calculated for each of the constituents and for each set of values of γ for O₂ and N₂. The height at which a particular value of N_2 occurs is obtained from the data given in table 1. The results are tabulated below.

TABLE 5.

(a) Ionisation Distribution due to Atomic Oxygen

N (Molecules per c. c.)	Height above ground (Km.)	Ionisation density (Electrons/c. c.)
10 ^{11.5}	155	10 ^{2.99}
10 ¹¹	191	10 ^{5.94}
10 ^{10.5}	228	10 ^{8.70}
10 ¹⁰	264	10 ^{8.77}
10 ⁹	336	10 ^{6.41}
10 ⁸	408	10 ^{5.92}
10 ⁶	554	10 ^{4.92}
10 ⁴	700	10 ^{3.92}

TABLE 5 (contd.).

(b) Ionisation Distribution due to O_2

N (Molecules per c.c.).	Height above ground (Km.).	Ionisation density (Electrons/c.c.)	
		(i) $\gamma = 10^{17.1597}$.	(ii) $\gamma = 10^{18.4607}$.
$10^{13.6}$	83.5	.	$10^{2.49}$
10^{13}	86	Very small	$10^{5.18}$
10^{12}	91	$10^{5.37}$	$10^{5.91}$
10^{11}	96	$10^{5.48}$	$10^{5.53}$
10^{10}	101	$10^{5.04}$	$10^{5.04}$
10^9	106	$10^{4.54}$	$10^{4.54}$
10^8	111	$10^{4.04}$	$10^4.04$
10^6	121	$10^3.04$	$10^{3.04}$
10^4	131	$10^2.04$	$10^{2.04}$

(c) Ionisation Distribution due to N_2

N (Molecules per c.c.).	Height above ground (Km.).	Ionisation Density (Electrons/c.c.).	
		(i) $\gamma = 10^{18.9053}$	(ii) $\gamma = 10^{18.2063}$
$10^{12.4}$	130	.	$10^{5.27}$
10^{12}	140	$10^7.51$	$10^{6.03}$
$10^{11.5}$	167	$10^{5.41}$	$10^{6.21}$
10^{11}	187	$10^5.84$	$10^{6.09}$
$10^{10.6}$	208	$10^{5.81}$	...
10^{10}	229	$10^{5.63}$	$10^{5.65}$
10^9	272	$10^{5.11}$	$10^{6.16}$
10^8	314	$10^4.66$	$10^4.66$
10^6	398	$10^3.66$	$10^3.66$
10^4	482	$10^2.66$	$10^2.66$

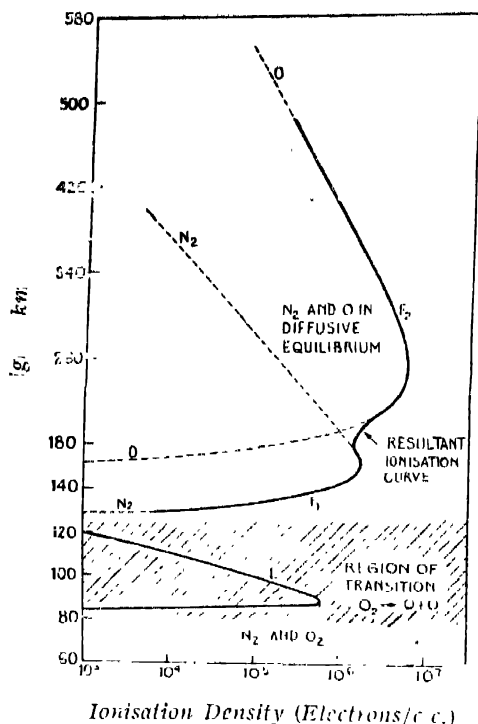


Fig. 2—Distribution of ionisation with height. $\gamma = 1/50 \gamma(\text{Kramers})$.

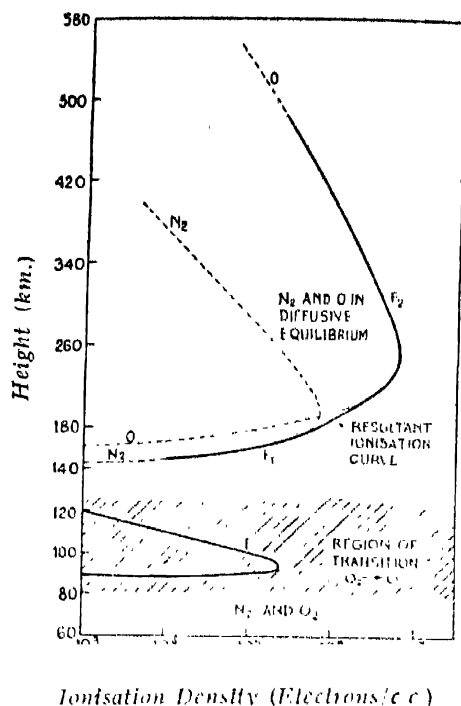


Fig. 3—Distribution of ionisation with height. $\gamma = 1/10 \gamma(\text{Kramers})$.

The results are plotted in figs. 2 and 3.

DISCUSSION OF RESULTS

As mentioned in section 4(b), on account of the uncertainty regarding the value of γ for O_2 and N_2 , we have assumed two possible different values of γ for these two gases. In figure 2 the values of γ for both O_2 and N_2 are taken as $1/50$ of the corresponding values obtained from Kramers' formula on the assumption that the value of Z (effective nuclear charge) for O_2 and N_2 are 8 and 7, respectively. It will be seen that the upper thick line curve in figure 2 which is the resultant of the two curves due to O and N_2 (obtained by adding the abscissae) shows two distinct ionisation maxima at the levels of 250 and 160 kms. approximately. The upper maximum evidently corresponds to region F_2 and the lower one to region F_1 . The respective electron densities are 6.3×10^6 and 1.6×10^6 per c.c. These values are to be regarded as those for equinoctial noon over the equator, *i.e.*, when the sun is directly overhead. With the variation of the solar activity the values of the ionisation density of all the layers will of course change enormously but it will be seen that the calculated values are of the correct order and also that the relative values of the maximum ionisation of the different layers as well as their heights agree closely to those actually observed.

The most interesting result of our calculations is with regard to the layer at about 100 km. level. There is no difficulty in identifying this with the E_1 layer the presence of which could not be hitherto explained theoretically. As mentioned in the introduction the position as well as the distribution of ionisation of this layer is determined by the existence of the region of transition of O_2 to O , the influence of which on the production of a layer of ionisation had not been considered till now. It will be noted that the layer is extremely thin; this is in conformity with experimental evidence. The calculated value of the ionisation density (6.3×10^5 electrons/c.c.) seems to be slightly in excess of the observed value, but this may possibly be due to the fact that the reduction of intensity in the band $\lambda\lambda 744-661\text{\AA}$ caused by the absorption of the overlying N_2 and O is greater than that assumed in section 5(b).

In figure 3, the values of γ for both O_2 and N_2 are taken to be $1/10$ of $\gamma(\text{Kramers})$. The resultant ionisation curve for the upper region (F layer) does not show the two stratifications F_1 and F_2 . Which of the two sets of values of the absorption coefficients [$1/50$ or $1/10$ of $\gamma(\text{Kramers})$] is more probable can only be decided by future experimental work on extreme ultra-violet absorption of these gases. It is to be noted that neither the height nor the distribution of ionisation of the layer at 100 km. (E_1 layer) is markedly affected by the assumed changes in the value of γ .

Without going through the whole series of calculations one can estimate how the position of the ionisation maximum will depend on the various factors, such as the temperature, the absorption coefficients and the pressure or density at the datum level.

The height at which the maximum ionisation for a given gas will occur is given by

$$z_{\max} = H \log_e N_0 H \gamma$$

where

$$H = kT/mg, \text{ the "scale height."}$$

Inspection of this formula shows that if γ is decreased the height will decrease. Thus if for the F_2 and F_1 layers, keeping γ for O constant, we decrease the value of γ for N_2 , the effect will be to produce a greater separation of the two maxima.

An increase of temperature of the atmosphere will involve a rise in the levels of maximum ionisation.

Further if the proportion of nitrogen molecules with respect to atomic oxygen at the datum level be smaller than that assumed before (*i.e.*, if N_0 for N_2 is smaller than the assumed value, N_0 for O being constant) the stratification will be more pronounced because the level of maximum ionisation for N_2 will be lowered down.

In the case of the ionisation due to O_2 , we have

$$z_{\max} = \frac{1}{\theta} \log_e \frac{N_0 \gamma}{\theta}.$$

The value of N_0 , the molecular density at the 80 km. level is known with fair accuracy. The value of θ will, however, vary with the assumed density at 130 km., where dissociation of O_2 is supposed to be practically complete. In our calculations we have taken the density at this level as 10^4 molecules/c.c., so that $\theta = 4.6 \times 10^{-6}$. If instead of 10^4 we take 10^8 molecules/c.c., θ becomes equal to 2.27×10^{-6} and hence the level of maximum ionisation rises to a height of about 110 km. for both the values of γ .

ACKNOWLEDGMENTS

The investigation was undertaken at the suggestion of Prof. S. K. Mitra, and I take this opportunity of thanking him sincerely for his keen interest in the work and for the help and guidance he gave me in the preparation of the paper.

My thanks are also due to Mr. S. P. Ghose, M.Sc., for checking some of the calculations.

WIRELESS LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE,
92, UPPER CIRCULAR ROAD,
CALCUTTA.

APPENDIX

(Reference page 17)

We have, from Kramers' law,

$$\gamma_{\nu_0} = \gamma \frac{\nu_0^3}{\nu^3}$$

mean value of γ between the limits ν_0 and ν' is given by

$$\begin{aligned} \gamma &= \frac{\gamma_{\nu_0} \int_{\nu_0}^{\nu'} \frac{\nu_0^3}{\nu^3} d\nu}{\nu' - \nu_0} \\ &= \frac{\gamma_{\nu_0} \cdot \nu_0}{2} \left[\frac{\nu' + \nu_0}{\nu'^2} \right] \end{aligned} \quad \dots (a)$$

For O_2 , $v_0 = 4.036 \times 10^{15}$ and $v' = 4.568 \times 10^{15}$ (Table 3). Hence from eqn. (a),

$$\gamma = 0.83 \gamma_{v_0}.$$

For N_2 , $v_0 = 4.568 \times 10^{15}$ and $v' = 5.128 \times 10^{15}$. Hence $\gamma = 0.84 \gamma_{v_0}$

For O, we have⁹

$$\gamma_v = \frac{\gamma_{v_0}}{3} \left(\frac{4v_0^3}{v^3} - \frac{v_0^4}{v^4} \right)$$

$\therefore$ mean value of γ between the limits v_0 and v' is given by

$$\begin{aligned} \gamma &= \frac{\gamma_{v_0}}{3} \frac{\int_{v_0}^{v'} \left(\frac{4v_0^3}{v^3} - \frac{v_0^4}{v^4} \right) dv}{v' - v_0} \\ &= \frac{\gamma_{v_0}}{3} \left[\frac{5}{3} \frac{v_0}{v' - v_0} - \frac{2v_0^3}{v'^2(v' - v_0)} + \frac{v_0^4}{3v'^3(v' - v_0)} \right] \quad \dots (b) \end{aligned}$$

And for O, $v_0 = 3.314 \times 10^{15}$ and $v' = 4.036 \times 10^{15}$, so that we get, from eqn (b),

$$\gamma = 0.77 \gamma_{v_0}.$$

REFERENCES

- ¹ Mitra and Bhar, *Science and Culture*, **1**, 782 (1936), Colwell and Friend, *Nature*, **137**, 782 (1936); Watson Watt and others, *Nature*, **137**, 866 (1936).
- ² Appleton and Piddington, *Proc. Roy. Soc.*, **4**, **164**, 467 (1938).
- ³ Appleton, *Nature*, **131**, 172 (1933).
- ⁴ Pannekoek, *Proc. Amsterdam Akad.*, **29**, 1165 (1926).
- ⁵ Woltjer, *Physica*, **5**, 406 (1925).
- ⁶ Chapman, *Proc. Roy. Soc.*, **1**, **132**, 353 (1931).
- ⁷ Chapman and Appleton, *Proc. I.R.E.*, **23**, 658 (1935).
- ⁸ Chapman, *Proc. Phys. Soc.*, **43**, 26 (1931).
- ⁹ Saha and Rai, *Proc. Nat. Inst. Sci. India*, **4**, 319 (1938).
- ¹⁰ Bhar, Paper No. 58, Mathematics and Physics Section, Indian Science Congress (January, 1938).

- ¹¹ Hulburt, *Phys. Rev.*, **53**, 544 (1938).
- ¹² Saha, *Phil. Mag.*, **40**, 772 (1920).
- ¹³ Saha and Sur, *Phil. Mag.*, **1**, 1025 (1926).
- ¹⁴ Milne, *Phil. Mag.*, **47**, 209 (1924).
- ¹⁵ Majumdar, *Ind. J. Phys.*, **21**, 75 (1938).
- ¹⁶ Martyn and Pulley, *Proc. Roy. Soc., A*, **164**, 455 (1936); Ghose, *M.Sc. Thesis* (1933), *Calcutta University*.
- ¹⁷ Saha, *Proc. Roy. Soc., A*, **160**, 155 (1937).
- ¹⁸ Kaplan, *Nature*, **141**, 1139 (1938).
- ¹⁹ Bernard, *Nature*, **141**, 1140 (1938).
- ²⁰ Hulburt and Maris, *Rev. Mod. Phys.*, **9**, 44 (1937).
- ²¹ Wildt, *Astro. Jour.*, **83**, 1 (1930).
- ²² Mitra and Rakshit, *Indian Jour. Phys.*, **12**, 47 (1938).
- ²³ Kramers, *Phil. Mag.*, **46**, 836 (1923).
- ²⁴ Page, *Nature*, **141**, 1137 (1938).
- ²⁵ *The Observatory*, **61**, 178 (1938).
- ²⁶ Saha, *Proc. Nat. Inst. Sci. India*, **1**, 217 (1935).
- ²⁷ Chapman and Price, *Reports on Progress in Physics*, **3**, 42 (1937).
- ²⁸ Worley and Jenkins, *Phys. Rev.*, **54**, 305 (1938).
- ²⁹ Hopfield, *Phys. Rev.*, **36**, 789 (1930).
- ³⁰ Takamine, Suga and Tanaka, *Sc. Pap. I.P.C.R.*, **34**, 854 (1938).
- ³¹ Price and Collins, *Phys. Rev.*, **48**, 714 (1935).

ON THE INTENSITY OF IONIZATION IN THE EARTH'S ATMOSPHERE *

By A. C. BANERJI

AND

P. L. BHATNAGAR

(Allahabad University.)

(Received for publication, October, 1938.)

ABSTRACT. Chapman has calculated the rate of ion-production and absorption of radiation in the earth's atmosphere assuming that isothermal condition prevails throughout the atmosphere and that the temperature is constant throughout. In spite of the fact that ionised layers are formed at a height 300 kms. and above, he has totally neglected the variation of gravity even at such heights. It is known that up to 11 kms. above the sea-level the atmosphere is in adiabatic state. It has been found by recent observers that between 40 kms and 60 kms. above sea-level there is a positive temperature gradient and between 60 kms. and 82 kms. there is a marked decrease of temperature. Between 82 kms. and 300 kms. above sea-level temperature increases more or less linearly with height.

In the present paper the atmosphere has been divided into three regions, *viz.*,

1. From 82 kms. to 300 kms. above sea-level in which the temperature is taken to increase linearly with the height and the variation of gravity has been taken account of
 2. From 11 kms. to 82 kms. above sea-level in which, in spite of the abnormalities of temperature between 40-82 kms. the temperature has been assumed to be constant and equal to its mean value 260° absolute in order to avoid complications in mathematical analysis
 3. Adiabatic region from sea-level to 11 kms. above sea-level.
- For each of the regions the formula for the intensity of ionization has been found.

1. Chapman ¹ has calculated the rate of ion production and absorption of radiation in the earth's atmosphere. He has assumed that the isothermal condition prevails throughout the atmosphere and he has taken the value of density at the height z above the sea-level to be

$$\rho = \rho_0 \text{Exp} \left(-\frac{z}{H} \right)$$

where ρ_0 is the density at the sea-level and H is the height of the homogeneous atmosphere. He has not taken account of variation of gravity, although observations show that we get ionised layers even at the heights of 300 kms. and above, and we cannot totally neglect the effect of variation at these heights.

* Communicated by the Indian Physical Society.

It has been observed ² that up to a height of 11 kms. above sea-level the atmosphere is in adiabatic state. The existence of an isothermal layer ³ above the adiabatic region up to a height of 40 kms. above sea level has been amply confirmed by observation. The temperature in this isothermal layer is found to be about 220° absolute. Between 40 kms. and 60 kms. there is a positive temperature gradient ⁴ upwards and at about 60 kms. temperature exceeds 400° absolute. Lindemann and Dobson ⁵ have suggested that this high temperature is due to the absorption of solar radiation by ozone in the earth's atmosphere. Whipple ⁶ also has found that the abnormal propagation of sound to great distances required a rising of temperature between 40 kms. and 60 kms. levels. Between 60 and 82 kms. there is a marked decrease of temperature, and at 82 kms. the temperature is as low as 160° absolute. Humphreys ⁷ has suggested that the noctilucent night clouds found to occur at 82 kms. were due to ice crystals formed at the low temperature of 160° absolute. Evidence of ionised strata has been obtained by Watson Watt ⁸ and others at the heights of 8.5, 9.3, 10.0 and 10.75 kms. above sea-level.

It is believed that the temperature increases ⁹ more or less linearly with the height between the levels 82 and 300 kms. The temperature at the height 82 kms. is about 160° abs. and at the height 300 kms. it is about 1,200° absolute. Cabannes ¹⁰ has found abundant evidence of the presence of molecular nitrogen, molecular oxygen and water vapour at heights between 200 and 300 kms. According to Martin and Pulley ¹¹ the mean molecular mass of atmosphere between 100 and 300 kms. is very nearly that of molecular nitrogen.

For the purpose of calculating the ion-production we shall divide the earth's atmosphere into three regions, *viz.*, I, II and III.

Region I extends from level 82 to the level 300 kms. We shall take account of variation of gravity and the temperature at a height ($z \leq h$) above sea-level is taken to be

$$T = \frac{T_h}{(h-a)} (z-a),$$

where T_h is the temperature at the height h which is 82 kms. T_h , as we have mentioned above, is about 160° absolute, and at a height 300 kms. above the sea-level, temperature is about 1,200° abs. We find 'a' to be about 48.0 kms. If p is the pressure, ρ the density and T absolute temperature at a height z we have

$$p = KT\rho$$

where $K = \frac{R}{\mu}$,

and R = universal gas constant (8.26×10^7 in c. g. s. units),
 μ = mean molecular weight (not greater than 30) in terms of weight of hydrogen atom,

Region II extends from level 11 kms. We have assumed the temperature to be constant throughout the region and taken the mean value to be 260° absolute. Abnormalities in the upper part of this region could not be treated separately as these will complicate the mathematical analysis to a great extent. We have also taken account of the variation of gravity in this region.

We have the relation $p = K_1 \rho$,

where $K_1 = K T = \frac{R T}{\mu}$ and $T = 260^{\circ}$ absolute and μ is not greater than 30 as before.

Region III extends from sea-level to 11 kms. above the sea-level. We have assumed that this region is in adiabatic condition.

In addition to the relation $p = K \rho^{\gamma} T$, where as before $K = \frac{R}{\mu}$, we have also the relation $p = K_2 \rho^{\gamma}$, where γ is the ratio of the two specific heats.

2.

R E G I O N I

(Kilometre 82 to kilometre 300.)

We have $p = K \rho^{\gamma} T$

and $T = T_h \frac{(z-a)}{(h-a)}$, where $h = 82$ kms.

Taking variation of gravity into account, we have

$$dp = - \frac{gr^2 \rho}{(r+z)^2} dz,$$

where r is the mean radius of the earth and g is the mean acceleration due to gravity at the sea-level.

From the above relations we get

$$\frac{dp}{p} = - \left[\frac{gr^2}{\lambda} \frac{1}{(z-a)(r+z)^2} + \frac{1}{(z-a)} \right] dz,$$

where $\lambda = \frac{K T_h}{h-a}$. Integrating we get

$$\rho = \text{const.} \cdot \frac{(z+r)^a}{(z+a)^{a+1}} \cdot \exp \left(- \frac{\beta r}{z-r} \right),$$

where $\alpha = \frac{gr^2}{\lambda(r+a)^2}$ and $\beta = \frac{gr}{\lambda(r+a)}$. Evaluating the constant of integration and taking ρ_h to be the density at the height h above the sea-level, we get

$$\begin{aligned}\rho &= \rho_h \left(\frac{h-a}{z-a} \right)^{\alpha+1} \left(\frac{z+r}{h+r} \right)^{\alpha} \exp \left\{ \beta \left(\frac{r}{h+r} - \frac{r}{z+r} \right) \right\} \quad \dots (1) \\ &= \rho_h \left(\frac{h-a}{z-a} \right)^{\alpha+1} \left[1 + \frac{z-h}{r+h} \right]^{\alpha} \exp \left\{ \beta r \frac{(z-h)}{(h+r)(z+r)} \right\}.\end{aligned}$$

Expanding the last two terms and neglecting the terms containing the powers of $\frac{z}{r}$ higher than the second and the terms comparatively smaller than $\frac{z^3}{r^3}$, viz.,

$\frac{h^3}{r^3}$, $\frac{z^2 h}{r^3}$ and $\frac{zh^2}{r^3}$, we get

$$\rho = \rho_h \left(\frac{h-a}{z-a} \right)^{\alpha+1} \left\{ 1 + \frac{A}{r} (z-h) + \frac{B}{2r^2} (z-h)^2 \right\}, \quad \dots (2)$$

where

$$A = \alpha + \beta - \frac{h}{r} (\alpha + 2\beta)$$

and

$$B = (\alpha + \beta)^2 - (\alpha + 2\beta).$$

Taking

$$r = 6368 \times 10^5 \text{ cms.}$$

$$g = 981 \text{ cms./sec}^2$$

$$\mu = 30 \text{ (taking the maximum value)}$$

$$K = \frac{8.26 \times 10^7}{30} \text{ c. g. s. units}$$

$$T_h = 160^\circ \text{ abs.}$$

$$h = 82 \times 10^5 \text{ cms.}$$

$$a = 48 \times 10^5 \text{ cms.}$$

We find

$$\lambda = 1.296 \times 10^2 \text{ cms./sec}^2$$

$$\alpha = 7.456 \text{ (numerical factor)}$$

$$\beta = 7.513 \text{ (numerical factor)}$$

$$A = 14.6797 \text{ (numerical factor)}$$

$$B = 201.418 \text{ (numerical factor)}$$

$$\frac{A}{r} = 2.305 \times 10^{-7} \text{ c. g. s. units}$$

$$\frac{B}{2r^2} = 2.483 \times 10^{-15} \text{ c. g. s. units.}$$

We write
$$F(z) = \left(\frac{z+r}{h+r} \right)^a \text{Exp} \left\{ \beta \left(\frac{r}{h+r} - \frac{r}{z+r} \right) \right\}$$

and
$$F_1(z) = 1 + \frac{A}{r} (z-h) + \frac{B}{2r^2} (z-h)^2.$$

We obtain the results given below.

z in cms.	F(z).	F ₁ (z).	error.
82 × 10 ⁵	1	1	0%
100 × 10 ⁵	1.040	1.0423	+ .22 %
150 × 10 ⁵	1.168	1.168	0%
200 × 10 ⁵	1.306	1.3066	+ .076%
250 × 10 ⁵	1.461	1.457	-.27 %
300 × 10 ⁵	1.632	1.6204	-.71 %

The above table shows that up to the level 300 kms. $F(z)$ does not differ from $F_1(z)$ by any appreciable amount and the approximation is quite valid. We can therefore write

$$\begin{aligned} \rho &= \rho_h \left(\frac{h-a}{z-a} \right)^{a+1} \left\{ 1 + \frac{A}{r} (z-h) + \frac{B}{2r^2} (z-h)^2 \right\} \\ &= \rho_h (h-a)^{a+1} \left\{ \frac{B}{2r^2} - \frac{1}{(z-a)^{a+1}} + \frac{C}{r(z-a)^a} + \frac{D}{(z-a)^{a+1}} \right\} \quad \dots (3) \end{aligned}$$

where $C = A - B \frac{h-a}{r} = 13.6047$ (numerical factor)

and $D = 1 - A \frac{h-a}{r} + \frac{B}{2} \frac{(h-a)}{r^2} = .9246$ (numerical factor).

Consider a beam of monochromatic ionising solar radiation of unit cross section and intensity S_i exterior to the earth's atmosphere, passing through the layer between z and $z-dz$ above the point of observation P and at an inclination χ to the vertical. As usual, assuming that the absorption is proportional to the intensity S at that height and to the mass of the air traversed, the change of intensity dS after crossing a layer of thickness dz will be given by

$$dS = NS \sec \chi \rho_h (h-a)^{a+1} \left\{ \frac{B}{2r^2 (z-a)^{a+1}} + \frac{C}{r(z-a)^a} + \frac{D}{(z-a)^{a+1}} \right\} dz, \quad \dots (4)$$

where χ is also the zenith distance of the sun at P assuming it to be on the noon meridian and N is the coefficient of absorption. On integrating we get,

$$S = E \text{Exp} \left[-N\rho_h \sec \chi (h-a)^{a+1} \left\{ \frac{B}{2r^2(a-2)} \frac{1}{(z-a)^{a-2}} + \frac{C}{r(a-1)} \frac{1}{(z-a)^{a+1}} + \frac{D}{a} \frac{1}{(z-a)^a} \right\} \right], \quad \dots (5)$$

where E is a constant.

When $z=l$, $S=S_l$ where l gives the limit of the effective atmosphere we have

$$E = S_l \text{Exp} \left[N\rho_h \sec \chi (h-a)^{a+1} \left\{ \frac{B}{2r^2(a-2)} \frac{1}{(l-a)^{a-2}} + \frac{C}{r(a-1)} \frac{1}{(l-a)^{a+1}} + \frac{D}{a} \frac{1}{(l-a)^a} \right\} \right] \quad \dots (6)$$

provided $F(z)$ does not materially differ from $F_1(z)$ when $z=l$.

If the number of the ions produced by absorption of unit quantity of the radiation be Q, the rate of production of ions per c.c. will be $Q \cos \chi \frac{dS}{dz}$, which will be denoted by $I(\chi, z)$. Hence

$$I(\chi, z) = QNE \rho_h \left(\frac{h-a}{z-a} \right)^{a+1} \left\{ 1 + \frac{A}{r} (z-h) + \frac{B}{2r^2} (z-h)^2 \right\} \times \\ \text{Exp} \left[-N\rho_h \sec \chi (h-a)^{a+1} \left\{ \frac{B}{2r^2(a-2)} \frac{1}{(z-a)^{a-2}} + \frac{C}{r(a-1)} \frac{1}{(z-a)^{a+1}} + \frac{D}{a} \frac{1}{(z-a)^a} \right\} \right],$$

by (2), (3), and (4).

If $I(\chi, h)$ is the value of $I(\chi, z)$ when $z=h$, we have

$$I(\chi, z) = I(\chi, h) \left(\frac{h-a}{z-a} \right)^{a+1} \left(\frac{z+r}{h+r} \right)^a \times \text{Exp} \left[\beta \left(\frac{r}{h+r} - \frac{r}{z+r} \right) \right. \\ \left. + N\rho_h \sec \chi \left\{ \left(\frac{B(h-a)^3}{2r^2(a-2)} + \frac{C(h-a)^2}{r(a-1)} + \frac{D}{a} (h-a) \right) - \left(\frac{h-a}{z-a} \right)^{a+1} \left(\frac{B(z-a)^3}{2r^2(a-2)} \right) \right\} \right]$$

$$+ \frac{C(z-a)^2}{r(a-1)} + \frac{D}{a} (z-a) \Bigg) \Bigg],$$

by writing $F(z)$ for $F_1(z)$ in the right hand expression.

We may put

$$I(x, z) = J I(x, h) \left(\frac{h-a}{z-a} \right)^{a+1} \left(\frac{z+r}{h+r} \right)^a \times \\ \text{Exp} \left[-\frac{\beta r}{r+z} - N\rho_h \sec \chi \left(\frac{h-a}{z-a} \right)^{a+1} \left\{ \frac{B(z-a)^3}{2r^2(a-2)} + \right. \right. \\ \left. \left. \frac{C(z-a)^2}{r(a-1)} + \frac{D(z-a)}{a} \right\} \right], \quad \dots (7)$$

$$\text{where } J = \text{Exp} \left[\frac{\beta r}{r+h} + N\rho_h \sec \chi \left\{ \frac{B(h-a)^3}{2r^2(a-2)} + \frac{C(h-a)^2}{r(a-1)} + \frac{D(h-a)}{a} \right\} \right]$$

$$= \text{Exp}[7.416 + N\rho_h \sec \chi \{4.625 \times 10^5\}], \text{ if } h=82 \text{ kms. and } a=48 \text{ kms.}$$

From (5) and (6) we also get, if S_h and S_l are values of S when $z=h$ and $z=l$,

$$S_h = S_l \text{Exp} \left[N\rho_h \sec \chi \left\{ \left(\frac{h-a}{l-a} \right)^{a+1} \left(\frac{B(l-a)^3}{2r^2(a-2)} + \frac{C(l-a)^2}{r(a-1)} + \frac{D(l-a)}{a} \right) - \right. \right. \\ \left. \left. \left(\frac{B(h-a)^3}{2r^2(a-2)} + \frac{C(h-a)^2}{r(a-1)} + \frac{D(h-a)}{a} \right) \right\} \right] \\ = S_l \text{Exp} [-N\rho_h \sec \chi \{4.625 \times 10^5\}], \text{ where } h=82 \text{ kms. and } \\ l=300 \text{ kms.} \quad \dots (8)$$

3.

REGION II

(Kilometre 11 to Kilometre 82.)

If the variation of gravity be neglected the formula of Chapman for the intensity of ionization will hold good for this region. In the following treatment we have taken into consideration the variation of gravity also. With the same notation as in the treatment of region I we have

$$\rho = \rho_d \text{Exp} \left[\frac{gr}{\kappa_1} \left\{ \left(1 + \frac{z}{r} \right)^{-1} - \left(1 + \frac{d}{r} \right)^{-1} \right\} \right], \quad \dots (9)$$

where ρ_d is the density at the height d where the isothermal region begins.

Here

$$K_1 = KT = \frac{RT}{\mu},$$

where R = universal gas constant (8.26×10^7)

μ = mean molecular weight (maximum value 30 for the neutral molecules of oxygen and nitrogen).

T = mean absolute temperature in the region (260° abs.)

Now $\frac{gr}{K_1} = 872.6$ approximately (numerical factor).

The highest value of z in this region is 82×10^5 cms and d is 11×10^5 cms.

Neglecting $\left(\frac{z}{r}\right)^3$ and smaller quantities we get

$$\begin{aligned} \rho &= \rho_d \text{Exp} \left[-\frac{gr}{K_1} (z-d) \right] \cdot \text{Exp} \left[\frac{gr}{K_1 r} (z^2 - d^2) \right] \\ &= \rho_d \left\{ 1 + a_1 \frac{z^2 - d^2}{r^2} \right\} \cdot \text{Exp} \left\{ -a_1 \frac{(z-d)}{r} \right\}, \quad \dots (10) \end{aligned}$$

where

$$a_1 = \frac{gr}{K_1}.$$

Let
$$\Phi(z) = \text{Exp} \left[\frac{gr}{K_1} \left\{ \left(1 + \frac{z}{r} \right)^{-1} - \left(1 + \frac{d}{r} \right)^{-1} \right\} \right]$$

and
$$\Phi_1(z) = \left\{ 1 + a_1 \frac{z^2 - d^2}{r^2} \right\} \text{Exp} \left\{ -a_1 \frac{(z-d)}{r} \right\}.$$

z in cms.	$\Phi_1(z)$.	$\Phi(z)$.	error.
11×10^5	1	1	0%
20×10^5	.2914	.2932	.61%
50×10^5	.00505	.0051	.98%
82×10^5	.00002046	.00002081	1.68%

The above table shows that up to 82 kilometres $\Phi_1(z)$ does not differ from $\Phi(z)$ by any appreciable amount and the approximation may be regarded as sufficiently valid.

If we would have taken gravity to be constant, instead of (9) we would get the equation

$$\rho = \rho_d \Phi_2(z),$$

where
$$\Phi_2(z) = \text{Exp} \left[-\frac{g}{K_1} (z-d) \right] = \text{Exp} \left[-a_1 \frac{(z-d)}{r} \right]$$

Hence we find that at 82 kms. $\Phi_2(z)$ differs from $\Phi(z)$ by 16% and at 50 kms. the difference is over 5%. Hence it is necessary to take account of variation of gravity.

As before,

$$dS = NS\rho_d \sec \chi \left\{ 1 + a_1 \frac{z^2 - d^2}{r^2} \right\} \text{Exp} \left\{ -a_1 \frac{z-d}{r} \right\} dz \quad \dots (11)$$

and
$$S = F \text{Exp} \left[-\frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2\frac{a_1 z}{r} + \frac{a_1^2}{r^2} (z^2 - d^2) \right\} \right. \\ \left. \text{Exp} \left\{ -a_1 \frac{z-d}{r} \right\} \right], \quad \dots (12)$$

where F is a constant.

When $z = d$, $S = S_d$, we get

$$F = S_d \text{Exp} \left[\frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + \frac{2a_1 d}{r} \right\} \right]. \quad \dots (13)$$

Now

$$I(\chi, z) = Q \cos \chi \frac{dS}{dz} \\ = FNQ\rho_d \left\{ 1 + a_1 \frac{(z^2 - d^2)}{r^2} \right\} \times \\ \text{Exp} \left[-a_1 \frac{(z-d)}{r} - \frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{z}{r} + a_1^2 \frac{(z^2 - d^2)}{r^2} \right\} \right] \times \\ \text{Exp} \left\{ -a_1 \frac{(z-d)}{r} \right\},$$

by (11) and (12).

If $I(\chi, d)$ is the value of $I(\chi, z)$ when $z = d$, we have

$$I(\chi, z) = I(\chi, d) \left\{ 1 + a_1 \frac{(z^2 - d^2)}{r^2} \right\} \times \\ \text{Exp} \left[-\frac{a_1(z-d)}{r} - \frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{z}{r} + a_1^2 \frac{(z^2 - d^2)}{r^2} \right\} \right] \times$$

$$\begin{aligned} & \text{Exp} \left\{ -a_1 \frac{(z-d)}{r} \right\} + \frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{d}{r} \right\} \Bigg] \\ &= I(\chi, d) \text{Exp} \left[a_1 \left(-\frac{r}{z+r} - \frac{r}{d+r} \right) + \frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{d}{r} \right\} \right. \\ & \quad \left. - \frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{z}{d} + a_1^2 \frac{(z^2-d^2)}{r^2} \right\} \right] \text{Exp} \left(-a_1 \frac{(z-d)}{r} \right), \end{aligned}$$

by writing $\Phi(z)$ for $\Phi_1(z)$. We may put

$$\begin{aligned} I(\chi, z) &= J_1 I(\chi, d) \times \\ & \quad \text{Exp} \left[\frac{a_1 r}{z+r} - \frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{z}{r} + a_1^2 \frac{(z^2-d^2)}{r^2} \right\} \right. \\ & \quad \left. \text{Exp} \left(-a_1 \frac{(z-d)}{r} \right) \right], \end{aligned} \quad \dots (14)$$

where

$$\begin{aligned} J_1 &= \text{Exp} \left[-\frac{a_1 r}{d+r} + \frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{d}{r} \right\} \right] \\ &= \text{Exp} [-871'2 + N\rho_d \sec \chi \{ 7'34 \times 10^5 \}], \text{ if } d = 11 \text{ kms.} \end{aligned}$$

If S_d and S_h are the values of S when $z=d$ and $z=h$, we have from (12) and (13),

$$\begin{aligned} S_d &= S_h \text{Exp} \left[\frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{h}{r} + a_1^2 \frac{(h^2-d^2)}{r^2} \right\} \times \right. \\ & \quad \left. \text{Exp} \left(-a_1 \frac{(h-d)}{r} \right) - \frac{rN\rho_d \sec \chi}{a_1^2} \left\{ a_1 + 2 + 2a_1 \frac{d}{r} \right\} \right] \\ &= S_h \text{Exp} [-N\rho_d \sec \chi (7'34 \times 10^5)] \end{aligned} \quad \dots (15)$$

REGION III

(Adiabatic region : sea-level to 11 kms.)

As maximum height is only 11 kms., we shall take gravity to be constant throughout this region. Here we have

$$p = K\rho T \text{ and } p = K_2\rho^\gamma,$$

where γ is the ratio of the two specific heats. Now if T_0 , ρ_0 and p_0 are the absolute temperature, density and pressure at the sea-level we have

$$\left(\frac{p}{p_0} \right)^{\gamma-1} = \frac{T}{T_0} = 1 - \frac{\gamma-1}{\gamma} \frac{\rho_0}{p_0} g z = 1 - a_2 \frac{z}{r}, \text{ where } z \leq d (= 11 \text{ kms.})$$

and

$$a_2 = \frac{\gamma-1}{\gamma} \frac{\rho_0}{p_0} g r = \frac{\gamma-1}{\gamma} \frac{r}{H},$$

where H is the height of the homogeneous atmosphere.

If $H = 8.4$ kms. and $\gamma = 1.4$, then $a_2 = 2.166$ (numerical factor) we have

$$\rho = \rho_0 \left\{ 1 - a_2 \frac{z}{r} \right\}^{\frac{1}{\gamma-1}}. \quad \dots (16)$$

$$\text{Now} \quad dS = NS\rho_0 \sec \chi \left\{ 1 - a_2 \frac{z}{r} \right\}^{\frac{1}{\gamma-1}} dz$$

$$\text{and} \quad S = G \text{Exp} \left[- \frac{rN\rho_0 \sec \chi (\gamma-1)}{\gamma a_2} \left(1 - a_2 \frac{z}{r} \right)^{\frac{\gamma}{\gamma-1}} \right],$$

where G is a constant.

We get

$$S = S_d \text{Exp} \left[\frac{rN\rho_0 \sec \chi (\gamma-1)}{\gamma a_2} \left\{ \left(1 - a_2 \frac{d}{r} \right)^{\frac{\gamma}{\gamma-1}} - \left(1 - a_2 \frac{z}{r} \right)^{\frac{\gamma}{\gamma-1}} \right\} \right] \dots (17)$$

Now

$$I(\chi, z) = Q \cos \chi \frac{dS}{dz} = S_d Q N \rho_0 \left(1 - a_2 \frac{z}{r} \right)^{\frac{1}{\gamma-1}} \times$$

$$\text{Exp} \left[\frac{rN\rho_0 \sec \chi (\gamma-1)}{\gamma a_2} \left\{ \left(1 - a_2 \frac{d}{r} \right)^{\frac{\gamma}{\gamma-1}} - \left(1 - a_2 \frac{z}{r} \right)^{\frac{\gamma}{\gamma-1}} \right\} \right].$$

If $I(\chi, 0)$ be the value of $I(\chi, z)$ at $z=0$, we have

$$I(\chi, z) = I(\chi, 0) \left(1 - a_2 \frac{z}{r} \right)^{\frac{1}{\gamma-1}} \times$$

$$\text{Exp} \left[\frac{rN\rho_0 \sec \chi (\gamma-1)}{\gamma a_2} \left\{ 1 - \left(1 - a_2 \frac{z}{r} \right)^{\frac{\gamma}{\gamma-1}} \right\} \right]. \quad \dots (18)$$

5. It may be observed here that S_d has been found in terms of S_h and S_h has been found in terms of S_l . If l gives the limit of the effective atmosphere, S_l has the same value as S_∞ in Chapman's paper.¹²

We have also

$$\rho_d = \rho_0 \left\{ 1 - a_2 \frac{d}{r} \right\}^{\frac{1}{\gamma-1}} = .31 \rho_0, \text{ if } d = 11 \text{ kms. and } \gamma = 1.4$$

and
$$\rho_h = \rho_d \text{Exp} \left[a_1 \left\{ \left(1 + \frac{h}{r} \right)^{-1} - \left(1 + \frac{d}{r} \right)^{-1} \right\} \right], \quad \text{by (16) and (9)}$$

$$= 2.081 \times 10^{-5} \rho_d, \text{ if } h = 82 \text{ kms.}$$

$$= 6.45 \times 10^{-6} \rho_0, \text{ where } \rho_0 \text{ is the density at the sea-level.}$$

From (15) and (8) we get

$$\begin{aligned} S_d &= S_h \text{Exp} [-N \rho_d \sec \chi (7.34 \times 10^5)] \\ &= S_l \text{Exp} [-N \sec \chi \{4.625 \times 10^5 \rho_h + 7.34 \times 10^5 \rho_d\}]. \end{aligned}$$

Our thanks are due to Prof. S. K. Mitra for his suggestions.

REFERENCES

- ¹ and ¹² Chapman, *Proc. Phy. Soc.*, **43**, 26 (1931).
- ² Jeans, *Dynamical Theory of Gases* (1916), p. 352.
- ³ to ⁷ and ⁹ to ¹¹ Martyn and Pulley, *Proc. Roy. Soc.*, **154**, 455 (1936).
- ⁸ Watson Watt, Wilkins and Bowen, *Proc. Roy. Soc.*, **161**, 181 (1937).

THE SPECTRUM OF ARGON IV

By A. BALANKESWARA RAO,
KOTCHERLAKOTA NARASINGARAO RESEARCH FELLOW,
Andhra University, Waltair.

(Received for publication, November 3, 1938.)

ABSTRACT. The spectrum of argon has been investigated under several experimental conditions in the near ultra-violet and visible regions. An examination of the data obtained enabled the extension of the analysis of the spectrum of the trebly ionised atom of argon into the visible and the near ultra-violet regions. A dozen terms have been newly discovered in the present investigation involving the classification of about 30 lines

INTRODUCTORY

Of the several spectra of argon, the analyses of A I¹ A II² and A III³ were investigated by various workers—Meissner, Compton, Boyce, De Bruin and others. But, of the spectrum of trebly ionised argon, A IV, only a partial analysis was done by Boyce,⁴ his investigation being confined to the very extreme ultra-violet vacuum grating region. With a view to further extending the analysis into the near ultra-violet and the visible regions, investigations on the spectrum of argon gas were undertaken from λ 2000 to λ 6000 under various experimental conditions and these enabled the detection of the prominent terms due to the $4p$, $4d$ configuration.

EXPERIMENTAL

The discharge tube employed for this work was just similar to that used with krypton.⁵ The same general experimental arrangement and procedure were adopted with argon, an argon reservoir being substituted in place of that containing krypton. A diagram of the discharge tube, the drying system of calcium chloride and potassium hydroxide towers, the vacuum pump, and the gas reservoir with its attachment is represented in figure I. The gas was excited by passing a condensed discharge through the tube, between aluminium electrodes with the help of a transformer capable of giving 20,000 volts in the secondary. A small inductance was used in series with the secondary circuit to suppress the lines due to the residual air. Photographs of the spectrum under different stages of excitation were obtained by taking recourse to the usual methods of altering the capacity, the length of the series gap and the pressure of the gas inside the tube. A Fuess glass spectrograph and a Hilger large Litrow type of quartz spectrograph were employed to obtain the spectrograms.

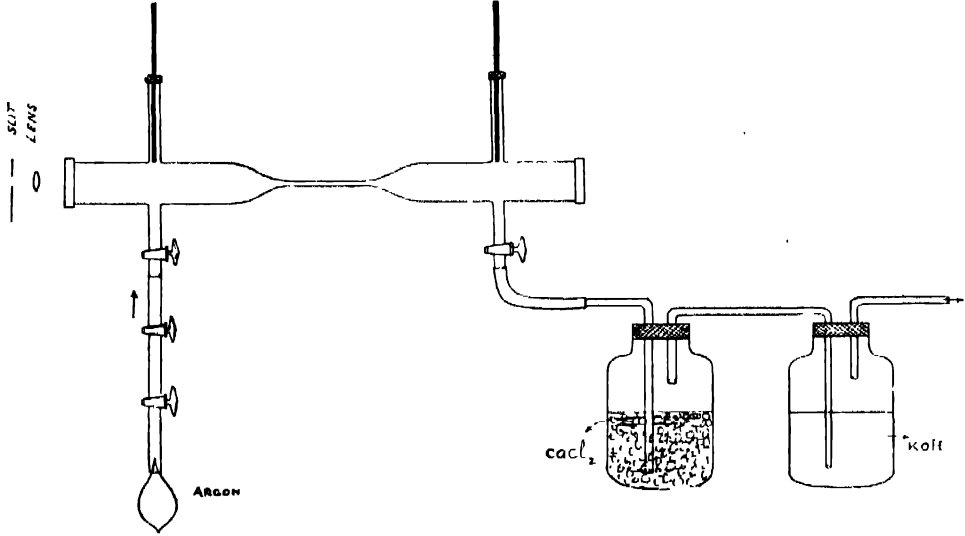


FIGURE 1
PREDICTED TERMS

The characteristic terms of the spectrum of A IV predicted theoretically in accordance with the theory of Hund and Heisenberg are presented in Table I.

Out of these the fundamental $4s\ (^4P-^4D)\ 4s^4P-4p^4P$ multiplets, and some doublet terms due to the $4p$, configurations were identified already by the previous workers. In the present work some of the prominent terms due to the $4p, 4d$ configurations have been detected.

TABLE I
Predicted Terms in Argon IV

CONFIGURATION.										Term Prefix.	Terms.
4 ₁	4 ₂	4 ₃	4 ₄	5 ₁	5 ₂	5 ₃	5 ₄	5 ₅	6 ₁		
2	3									4 ^p	4S 2D 2P
2	2									5 ^s	4P 2P 2D 2S 4D 4P 4S 2F 2D ^a 2P ^b
2	2									5 ^p	2D 2P 2S 2P ^a
2	2									4 ^d	4F 4D 4P 2G 2F ^a 2D ^a 2G ^b 2F 2D 2P 2P ^a 2S ^b
2	2									6 ^s	4P 2P 2D 2S
1	4									5 ^{p4}	4P 2P 2D 2S

TABLE II
Multiplet Scheme in Argon IV

$4p$	$4D_{\frac{1}{2}}$	$4D_{\frac{3}{2}}$	$4D_{\frac{5}{2}}$	$4D_{\frac{7}{2}}$	$4P_{\frac{1}{2}}$	$4P_{\frac{3}{2}}$	$4P_{\frac{5}{2}}$	$4S_{\frac{1}{2}}$
$4s$	283960	186228.8	286751.7	287555.8	289125.9	289237.8	289834.7	291748.7
$4P_{\frac{1}{2}} = 230219$ 687.1	$35740.7 (7)$	$36009.1 (10)$			$38905.9 (7)$	$39018.7 (12)$		$41529.4 (6)$
$4P_{\frac{1}{2}} = 230906.6$ 1066	$35053.6 (4)$	$35222.2 (10)$	$35845.1 (14)$		$38219.3 (12)$	$38331.2 (10)$	$38928.1 (10)$	$40842.1 (8)$
$4P_{\frac{3}{2}} = 231972$		$34256.8 (3)$	$34719.7 (16)$	$35583.8 (16)$		$3765.8 (9)$	$37862.6 (15)$	$39776.7 (12)$
$2P_{\frac{1}{2}} = 256093.3$					$33032.6 (5)$	$33145.2 (5)$		
$2P_{\frac{1}{2}} = 257348.9$					$31776.9 (4)$	$31889.7 (3)$	$32485.6 (8)$	
$2D_{\frac{1}{2}} = 268171.4$								
$2D_{\frac{3}{2}} = 268151.4$					$42507.6 (1)$	$42623.6 (5)$	$30068.6 (6)$	$31980.7 (2)$
$a = 246616$		$26464.9 (4)$				$29473.9 (8)$		
$b = 259765$	$32615.8 (1)$	$32887.9 (2)$				$35890.9 (4)$		
$c = 253344$	$29193.7 (5)$	$29461. (2)$						
$d = 256767$	$26653.5 (6)$	$26923.3 (6)$						
$e = 259306$	$23635.1 (8)$	$23899.7 (6)$						
$f = 262327$	$22631.9 (2)$	$22904.1 (3)$						
$g = 263327$	$21280.5 (3)$	$21548.7 (1)$			$24448.7 (3)$	$25009.8 (7)$		$27072.5 (4)$
$h = 264678$	$20520.8 (2)$	$20790.0 (2)$	$21311.9 (2)$					$26305.6 (5)$
$i = 265440$	$17147.9 (5)$	$14417.0 (4)$			$20310.3 (1)$	$20425.3 (3)$		
$j = 268813$	$16836.0 (2)$	$17098.0 (5)$						
$k = 269127$								

ANALYSIS

A careful examination of the plates taken under different excitations made it possible to ascribe about a hundred lines as belonging to the trebly ionised atom of argon and of these, about 30 lines have entered into the extension of the multiplet scheme of argon suggested in this work. Many of the lines are rather broad and broader than those due to krypton under similar experimental conditions. This might probably be due to the smaller atomic weight of argon. The difficulty of measurement of the argon lines was therefore larger and the accuracy somewhat less than that obtained with krypton lines.

The working out of the analysis of A IV was comparatively easier than that of Kr IV as the differences involved are smaller and as the structure and the main intervals are known from the work of de Bruin and Boyce. A search was made for the pairs having the wave-number differences 268.6 and 111.9 cm^{-1} corresponding respectively to $4p\ (^4D_{\frac{1}{2}} - ^1D_{1\frac{1}{2}})$ and $4p\ (^4P_{\frac{1}{2}} - ^4P_{1\frac{1}{2}})$. The selections of the proper pairs from these was made by trying to extend the scheme with each of these pairs. Starting then with some of the cross differences, new levels could be detected. Thus a new level scheme was set up and shown in Table II which includes also the combinations identified by Boyce.

About a dozen levels have been thus newly identified and these are expected to be due chiefly to the md configuration. They are designated arbitrarily by the symbols a, b, c, etc., as it is practically impossible to make a more definite assignment or even to distinguish between the quartet and doublet terms. The proper value of even the inner quantum number of these levels cannot be defined unambiguously. The values suggested in certain cases are to be regarded as tentative. But it is believed that the levels themselves are all real. Table III shows the list of lines newly classified in the spectrum of argon IV.

TABLE III

Newly classified lines in Argon IV

λ (Snt.),	ν (vac.),	Classification	ν (Snt.),	ν (vac.),	Classification.
5938.01(2)	16836.0	$4p^4D_{\frac{1}{2}} - k$	3750.79(6)	26653.5	$4p^4D_{\frac{1}{2}} - e$
5847.03(5)	17008.0	$4p^4D_{1\frac{1}{2}} - k$	3713.19(6)	26923.3	$4p^4D_{1\frac{1}{2}} - e$
5830.04(5)	17147.9	$4p^4D_{\frac{1}{2}} - j$	3692.74(4)	27072.5	$2p^4S_{1\frac{1}{2}} - h$
5739.88(4)	17417.2	$4p^4D_{1\frac{1}{2}} - j$	3424.13(5)	29193.7	$4p^4D_{\frac{1}{2}} - d$
4922.50(1)	20310.3	$4p^4P_{\frac{1}{2}} - j$	3393.35(2)	29461.0	$4p^4D_{1\frac{1}{2}} - d$
4894.53(3)	20425.3	$4p^4P_{1\frac{1}{2}} - j$	3391.86(8)	29473.9	$4p^2P_{\frac{1}{2}} - b$

TABLE III (contd.)

Newly classified lines in Argon IV

$\lambda(\text{Å.})$	$\nu(\text{vac.})$	Classification	$\nu(\text{Sut.})$	$\nu(\text{vac.})$	Classification.
4871.78(2)	20520.8	$4p^4D_{1\frac{1}{2}}-i$	3324.78(6)	30068.6	$4p^4P_{2\frac{1}{2}}-b$
4808.66(2)	20790.0	$4p^4D_{1\frac{1}{2}}-i$	3157.60(3)	36660.6	A-b
4697.87(3)	21280.5	$4p^4D_{\frac{3}{2}}-h$	3125.98(2)	31980.7	$4p^4S_{1\frac{1}{2}}-b$
4690.9(2)	21311.9	$4p^4D_{2\frac{1}{2}}-i$	3065.11(1)	32615.8	$4p^4D_{\frac{1}{2}}-c$
4630.36(1)	21548.7	$4p^4D_{1\frac{1}{2}}-h$	3039.75 2'	32887.9	$4p^4D_{1\frac{1}{2}}-c$
4417.30(2)	22631.9	$4p^4D_{\frac{1}{2}}-g$	2985.04(1)	33490.6	$4p^4D_{1\frac{1}{2}}-d$
4364.80(2)	22904.1	$4p^4D_{2\frac{1}{2}}-g$	2785.30(4)	35890.9	$4p^4P_{1\frac{1}{2}}-c$
4279.81(8)	23635.1	$4p^4D_{\frac{3}{2}}-f$	2534.11(2)	39149.0	A- $4s^2P_{2\frac{1}{2}}$
4182.97(6)	23899.7	$4p^4D_{\frac{3}{2}}-f$	2467.3 3)	40517.6	A- $4s^2P_{1\frac{1}{2}}$
4089.04(3)	2418.7	$4p^4P_{\frac{1}{2}}-h$	2351.8(1)	42507.6	$4p^2p_{\frac{1}{2}}-a$
3908.43(2)	25578.5	$4p^2D_{2\frac{1}{2}}-h$	2345.4(5)	42623.6	$4p^4P_{1\frac{1}{2}}-a$
3858.46(6)	25900.8	$4p^4P_{1\frac{1}{2}}-g$			
3800.42(5)	26305.6	$4p^4S_{1\frac{1}{2}}-i$			
3777.52(4)	26464.9	$4p^4D_{1\frac{1}{2}}-f$			

Term Values

The term values are determined through the identified lines on the basis of the term scheme set up by Boyce in adopting $4s^2P_{\frac{1}{2}}$ equal to zero. Table IV shows completely all the values of the energy states so far known.

TABLE IV

Term Values in A IV

Term.	Term Value ν	$\delta\nu$	Term.	Term Value λ	$\delta\nu$
$4p^4D_{\frac{1}{2}}$	285960.2	268.6	A	291425.5	
$2D_{1\frac{1}{2}}$	286228.8	522.9			
$2D_{2\frac{1}{2}}$	286751.7	804.1	a	246616	
$2D_{5\frac{1}{2}}$	287555.8		b	259765	
			c	253344	

TABLE IV (contd.)

Term Values in A IV

Term.	Term Value. ν	$\delta\nu$	Term.	Term Value. λ	$\delta\nu$.
$2P_{\frac{1}{2}}$	289125.9		d	256767	
$2P_{\frac{3}{2}}$	289237.8	111.9	e	259306	
$4P_{\frac{1}{2}}$	289834.7	596.9	f	262327	
$2S_{\frac{1}{2}}$	291748.7		g	263327	
$2D_{\frac{1}{2}}$	290256.5		h	264678	
$2D_{\frac{3}{2}}$	291667.7	1411.2	i	265440	
$2P_{\frac{1}{2}}$	295674.5		j	268813	
$2P_{\frac{3}{2}}$	295805.8	131.3	k	269127	
$2S_{\frac{3}{2}}$	299663.2				
$2F_{\frac{5}{2}}$	304074.3				
$2F_{\frac{7}{2}}$	304370.9	325.6			
$4s4P_{\frac{1}{2}}$	250219				
$4P_{\frac{1}{2}}$	250906	687			
$4P_{\frac{3}{2}}$	251972	1066			
$2P_{\frac{1}{2}}$	256093.3				
$2P_{\frac{3}{2}}$	257348.8	1255.6			
$2D_{\frac{1}{2}}$	286171.4				
$2D_{\frac{3}{2}}$	268151.4	20			

In conclusion the author wishes to express his grateful thanks to Dr. K. R. Rao for his guidance and to Dr. S. G. Krishnamurty for helpful suggestions. He is indebted to the Andhra University for the award of a fellowship which has enabled him to carry out the above work.

REFERENCES

- 1 Meissner; *Zeits. f. Physik*, **39**, 172 (1926); *Ibid.*, **40**, 839 (1926).
- 2 de Bruin, *Zeits. f. Physik* **61**, 307 (1930).
- 3 de Bruin, T. L., *Proc. Amst. Acad.*, **36**, 724 (1933); Royce J. C., *Phys. Rev.*, **48**, 396 (1935).
- 4 *Ibid.*
- 5 Communicated to the Physical Society, London.

ON THE EXCITATION OF CHLADNI FIGURES

By L. SIBAIYA, M.Sc., F.A.Sc.

From the Department of Physics, Central College, Bangalore.

(Received for publication, November 9, 1938.)

Plate XI

The Chladni figures on plates of various shapes which are centrally fixed are usually obtained by sprinkling sand or lycopodium powder on the plates and exciting them by bowing. Various patterns are produced by changing the bowing point and the nodal point. Oscillatory circuits whose frequencies could be continuously varied have also been employed by Colwell¹ for exciting the plates. This method, though satisfactory, is rather elaborate for demonstration purposes. A simple mode of exciting the plate at any given point not necessarily on the periphery is as follows: A brass rod is clamped firmly at its mid-point and placed vertically with one of its sharp ends resting lightly on the plate at the given point. The rod is as usual stroked with a resined flannel cloth and is excited to vibrate longitudinally. It is found that the plate is excited and the note is one of the free frequencies of the plate corresponding to the point of excitation and is not that of the bar. This would show that the periodicity of the friction at stroking is governed by the plate and the rod serves mainly as a vehicle of energy, actually being in forced oscillation. The excitation is easier, if by loading the rod or adjusting its length, its free frequency is brought near that sought to be excited in the plate. The plate is thus easily excited to yield its various vibration patterns strongly and consistently. Tinsel powder is found most suitable for photographing the patterns. Figure 1 gives one of the many vibration patterns obtained by using a square plate centrally fixed; figure 2 gives the four concentric nodal circles (with the finer particles lying at the antinodal arcs) in the circular plate centrally clamped. Because of the large amount of energy that could be transmitted from the rod to any vibrating system, it has been found possible to study the vibration patterns of the sound-board (belly) of a vīna. This musical instrument (Fig. 3) peculiar to India and according to Fox Strangways (Encyclop. Britt. 14th Edn., Vol. 12, p. 241) consists of "three drone strings and four fretted strings on the finger board, plucked like, and with the tone of guitar." Figure 3, where the end of the bar is resting on the bridge,

gives the simplest mode of vibration wherein the circumference of the wooden belly forms a nodal curve. Figure 4 gives one of the many complex modes of vibration of the sound-board of the vīna. The experimental arrangement is shown in figure 4.

In this connection I wish to record a type of musical drone used by certain beggars in South India. A suitable metal plate of bronze resembling a dinner plate is slightly waxed near the centre on the outside and a reed is held in contact with the plate on the wax which prevents the reed from slipping. The performer after properly supporting the plate on the lap strokes the reed with both hands and produces a rich drone. Here, as in the experiment above, the reed is but a vehicle of energy and is itself more often in forced oscillation. The periodicity of friction at the stroking is governed by the free frequency of the plate.

I thank Professor A. Venkat Rao Telang for his helpful suggestions during the progress of the work.

R E F E R E N C E

- ¹ Colwell, *Phil. Mag* , **12**, 320 (1931); **15**, 317 (1933).

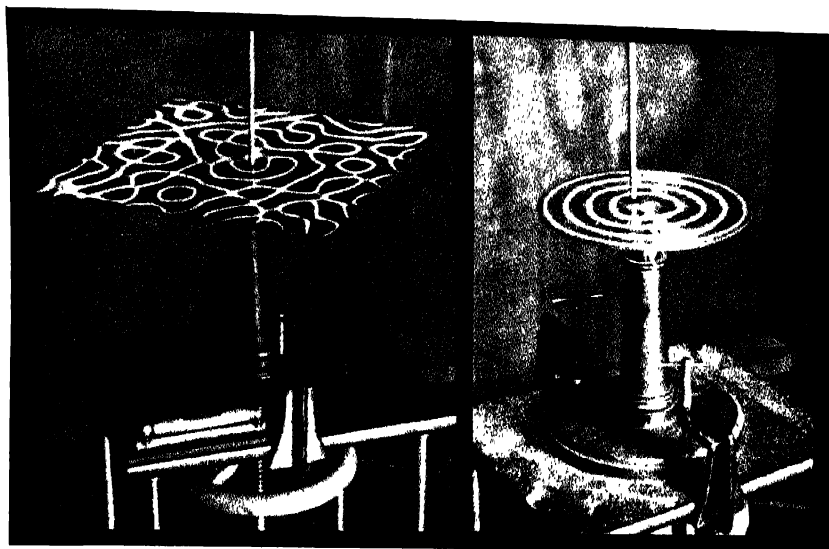


Fig. 1

Fig. 2

Fig. 3

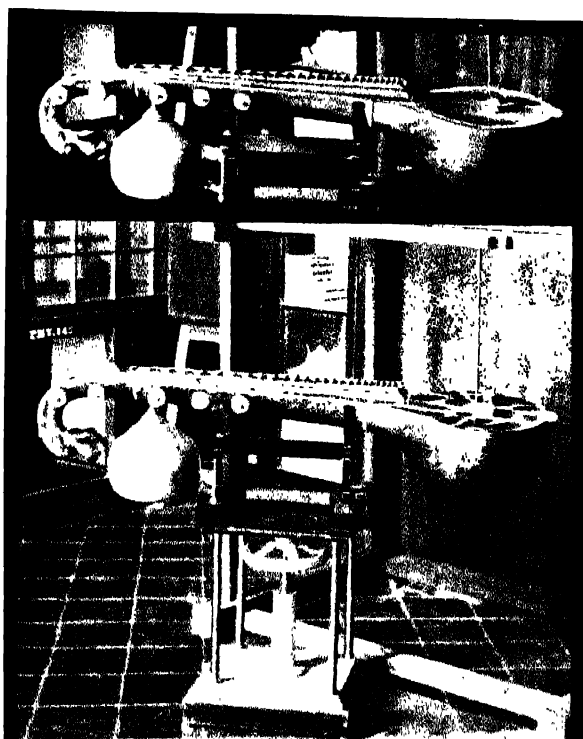


Fig.

ON THE INTERCHANGE OF ELECTRICITY BETWEEN SOLIDS, LIQUIDS AND GASES IN MECHANICAL ACTIONS *

By S. K. BANERJI, D.Sc., F.N.I.

(Received for publication, Nov. 19, 1938.)

ABSTRACT. When liquids or solid particles are subjected to various mechanical processes, such as frictional force, spraying, splashing, raining or blowing, striking against each other, etc., electric charges are developed in the substance, in the apparatus used in the mechanical process and in the surrounding medium. Similarly, some gas jets produce positive charge and others negative charge on the nozzle or on the plate on which they impinge. We have no complete picture for any one case to show how the interchange of electricity takes place between the apparatus, substance and the medium; consequently, experiments were undertaken with a number of substances, initially uncharged and initially charged, to supplement the observations made by previous workers. These show, as one should expect, that —

(1) The total charge in the substance, in the apparatus (or escaping into earth through the apparatus) and the medium in any mechanical process is zero. While the total remains zero, the distribution between the apparatus, substance and the medium (positive and negative ions) shows wide variations according to the process employed and the substance used. If the operation produces in any case equal number of positive and negative ions in the medium, the substance and the apparatus either collectively or separately remain uncharged.

(2) The charge developed depends on the violence of the mechanical action. Only a part of the work done in such processes is converted into electricity.

If the existence of an electrical double-layer between the substance and the medium is assumed, the ions in the medium come from both layers of the double-layer, but generally more from the layer situated on the molecules of the medium. The more violent is the process the greater is the number of ions dislodged from the layer situated on the molecules of the substance.

If a substance has an initial charge, this charge does not play any part in the interchange of electricity between it and the medium. The initial charge adheres to the substance during the process of disruption.

The exchange of electricity between substance and medium in all mechanical actions can be explained on the assumption of an electrical double-layer.

When increasing quantities of NaCl or HCl are dissolved in distilled water, the charge in the substance changes very sharply from positive to negative at a very low concentration. The distribution in such cases of charge in the substance, in the apparatus, and in the air in the shape of positive and negative ions is discussed particularly at the stage when the transition from positive to negative takes place. When the substance passes through the transition point, a reversal of the double-layer takes place.

* Communicated by the Indian Physical Society.

The interchange of electricity brought into play in some of the mechanical actions in the atmosphere is briefly considered and it is indicated that some of the earlier calculations need revision.

The various factors which contribute to the generation of charge in such processes and the possible genesis of the electrical double-layer on the electronic theory of matter are briefly discussed.

PART I—EXPERIMENTAL DATA

I. INTRODUCTION

A number of workers have carried out experiments on the electric charge developed when liquid drops (organic or inorganic) and solid particles are subjected to mechanical processes of various types. These involved spraying or splashing of liquids and raining or blowing of dust particles and in most cases attempt was made to explain the observed results on the assumption of an electrical double-layer. Unfortunately, we have no complete information for any case; those who have measured the charge on the substances have in most cases not recorded the charge in the medium or in the instruments employed and those who have recorded the charge in the medium have not noted the charge in the substances. Consequently, the precise rôle of the double-layer in the interchange of electric charge between the substance and medium when the former is subjected to breaking or friction has received no satisfactory elucidation.

The colloidal chemists assume electric charge to be a fundamental property of the colloidal particles. The existence of an electrical double-layer is assumed and the charge is supposed to have arisen as a result of 'slipping' of this double-layer. According to Mukherjee,¹ the inner layer forms a firmly adhering charge.

A simple experiment shows that aerosols have not necessarily a charge initially. If a jet of condensed steam is allowed to escape between two metal plates, placed 20 cm. apart, and charged to a potential difference of 50,000 volts, the steam is found to remain unaffected. If, on the other hand, the jet is subjected to a beam of X-rays, before it escapes between the two plates, the condensed steam is found to be highly charged and is attracted to one or the other of the plates according to its polarity. If the vapour particles in the jet be regarded as aerosols, then clearly the experiment shows that initially they are not charged. In other words, no slipping of the double-layer has occurred, and each particle is, therefore, uncharged.

Two fundamental questions arise—

(a) Is the assumption of the existence of a double-layer essential for the explanation of the development of electric charge in all mechanical processes?

(b) What is the precise rôle of the double-layer in the development of such charges?

We propose to examine both these questions with the aid of data obtained by previous workers on the subject and those obtained by the author with the assistance of a co-worker, Mr. R. D. Godbole, in order to supply the missing link.

2. AVAILABLE DATA

In 1892 Lenard² showed that water jets or drops striking against an obstacle are charged positively, while the surrounding air becomes negatively charged; the effect being reduced considerably by the presence of even slight impurities in the liquid used. A very important contribution was made by J. J. Thomson³ in 1894 when he brought to notice that the electrification of drops of distilled water striking against a metal surface suffers a reversal when hydrogen is substituted for air. In the literature of colloidal particles we find that substances of higher dielectric constant with respect to the medium get positively charged. This is clearly not true for breaking water drops, for, water has a higher dielectric constant both with respect to air and hydrogen, and yet in air the drops get positively charged and in hydrogen negatively charged.

Thomson showed that solutions such as phenol, pyrogallie acid, fluoresceine, whose drops are electrified in the same way as those of water are affected by hydrogen in the same way as drops of water are affected, *i.e.*, drops which would be positively charged in air would become negatively charged in hydrogen. On the other hand, the effect of substituting hydrogen for air in the case of substances like methyl violet, rosaniline, potassium permanganate, whose drops show negative electrification in air is to increase this negative electrification. If experiments are made with different gases the magnitude of the charge is found to depend largely on the amount of gas absorbed by the drops, by which they are surrounded. Thus, water falling through sulphuretted hydrogen gives very little charge, while water falling through its own vapour gives no effect. The temperature of the substance is also a factor of considerable influence. Thus, while water at 15°C, allowed to strike a plate gave a deflection of 230 scale divisions in the electrometer, that at 75°C and 95°C produced deflections of 390 and 420 divisions respectively.

Evic⁴ has made available to us a considerable amount of data in regard to the ionisation produced in the air by spraying different liquids. Unfortunately, he kept no record of the charge in the substance or in the apparatus. His results show that generally both positive and negative ions are produced by spraying, and that the number of the ions and the ratio of the negative to positive ions are characteristic of the substance sprayed. He also found that surface tension and the extent to which liquids are volatile do not appear to influence the relative ionisabilities of different substances. Busse⁵ showed that the production of positive ions takes place in a greater quantity in the case of spraying of water (the

ratio of positive ions to negative ions being about 2 : 3) than in the case of striking and bubbling processes (the ratio in these cases being roughly 1 : 15).

Nolan⁶ investigated the dependance of the separation of electrical charge on the surface produced, by measuring the charge on various sizes of drops produced by splashing and spraying water. If the charge developed (Q) be expressed in the form $Q = \sigma A$, where A is the area of the surface, then $\sigma = 2.5 \times 10^{-3}$ e.s.u./cm.²

Rudge⁷ showed that when dust particles are blown, the sign of the charge depended on the nature of the substance, *e.g.*, acidic bodies and non-metallic elements gave positively charged clouds, while basic bodies and metallic elements gave negatively charged clouds. The electrification of dust and air was in general, but not in every case, found to be of opposite sign. Deodar's tests⁸ on graded dust of different sizes showed that, other things being equal, the charge developed by blowing increased very rapidly as the size decreased. The charge also depended on the nature of the substance used. For instance, while NaCl and KCl were equally efficacious, NaNO_3 was about $1\frac{1}{2}$ times more efficacious in producing charge than KNO_3 .

3. FURTHER EXPERIMENTS

It will be seen from the above review that although a considerable series of experiments have been carried out on the subject, no author has recorded the charge in the substance, in the air and in the apparatus used for producing mechanical action. For instance, when water is sprayed, electric charge is developed in the sprayer, in the sprayed water drops, as well as in the surrounding air. Except in the case of water, we have no quantitative values of the charge in the substance and that in the medium in any particular operation. For water drops broken in a vertical blast of air, Simpson⁹ recorded the charge both in the substance as well as in the air. In order to get connected records of the total charge developed in such processes, it became necessary to carry out further experiments in which arrangements were made for recording the charge in the substance, in the air, as well as in the apparatus.

The mechanical processes employed for the development of charge were the following :—

In the case of liquids—

- (a) Drops broken in a vertical blast of air,
- (b) Drops striking a plate,
- (c) Jet striking a plate,
- (d) Two jets striking against each other in the air,
- (e) Spraying by an atomiser.

In the case of solid particles—

- (a) Particles raining through sieve and received on a plate,
- (b) Particles blown in the form of a cloud,
- (c) Particles slipping down two inclined planes and striking against each other in the air.

In the case of gas—

- (a) A gas jet striking a plate,
- (b) Two gas jets striking against each other.

In most cases the mechanical process was made automatic so that the same effect could be repeated as many times as desired.

The experimental arrangement usually adopted for spraying experiments is as shown in Fig. 1. For most of the experiments the receiver used was made out of an aluminium sheet. It was of a rectangular shape (6 in. $\times$ 3½ in. $\times$ 3¼ in.) with a circular tube of diameter 1½ in., length 2 in., fixed in the middle of a vertical side. It had a top cover which could be removed when necessary. Suitable modification is made in the receiver when experiments are made with jets or solid particles.

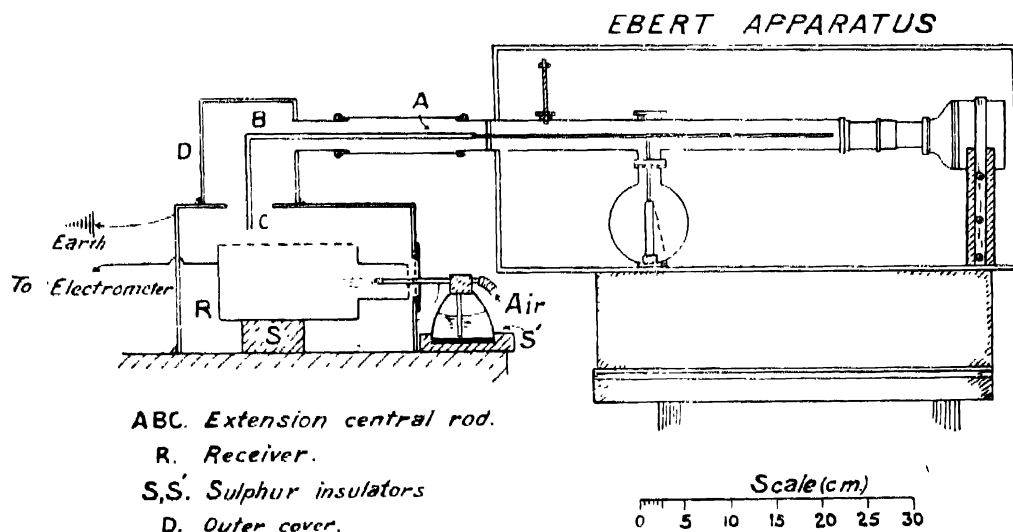


FIGURE 1

The substance subjected to the mechanical process is received in an insulated receiver which is connected to the needle of a Dolezalek electrometer, the quadrants being given equal and opposite potentials. The mechanical process occurs in an enclosed space, the air being subsequently drawn through an Ebert's counter, and the number of both positive and negative ions counted in two separate experiments.

When it is desired to measure also the charge on the apparatus, the receiver and the electrometer are earthed, the receiver is disconnected and the apparatus is joined to the electrometer.

The observations are taken in the order as described below.

Taking, for instance, the case of water sprayed, the spraying is done automatically by a motor blower. The nozzle of the atomizer is surrounded on all sides by the receiver, so that all the sprayed particles are collected by the receiver. A definite quantity of water, say 1 c.c., is sprayed every time and tests are made to see that the same effect is reproduced every time.

(1) First with a given (a) positive and (b) negative potential being applied instantaneously to the central rod of the Ebert's ion-counter, two leakage curves are drawn, with the fan working in the two cases.

(2) A definite quantity, say 1 c.c., of water is sprayed.

(3) The charge on the water collected in the receiver, as recorded by the Dolezalek electrometer is noted.

(4) The central rod of the ion-counter is given a definite positive potential.

(5) The air from the receiver is sucked in through the counter, by making the fan of the counter work, and a leakage curve is drawn.

(6) The drop in potential, as given by the two curves (5) and (1), gives, with the aid of the usual formula for Ebert's counter, the number of negative ions produced in the air by spraying 1 c.c. of water. Since both the leakage curves are equally affected by the ions normally present in air, these are automatically eliminated from the counting.

(7) With the receiver and the central rod momentarily earthed, 1 c.c. of water is again sprayed, and the charge acquired by the receiver, as recorded by the electrometer, noted.

(8) The central rod of the counter is now given a definite negative potential.

(9) The air from the receiver is sucked in and a leakage curve drawn.

(10) The drop in potential as shown by (9) and (1), gives the number of positive ions in the air as a result of spraying 1 c.c. of water.

(11) The receiver is earthed and disconnected, the apparatus is joined to the electrometer and the charge developed in it is noted.

For these experiments, both the Dolezalek electrometer and Ebert's ion-counter (with its Woulf's electrometer) are calibrated, the capacities of both and of the accessories being determined by means of a standard condenser.

PART II—SUBSTANCES INITIALLY UNCHARGED

4. We have to consider two distinct cases—substances may be initially charged or uncharged and it is best to treat them separately. We first take up the case of substances which are initially uncharged.

When a substance is subjected to mechanical action, we find electric charge in the apparatus employed to produce mechanical action as well as in the substance and the medium. For instance, water passing through the nozzle of the atomizer gives negative charge to the atomizer and itself acquires a positive charge. A further development of charge takes place while the jet breaks into fine drops and falls into the receiver, owing to the dislodgment of ions which escape into the medium. Thus if x is the charge developed in the apparatus, the charge in the substance when it just comes out of the apparatus is $-x$. If y is the resultant charge given to the medium as a result of dislodgment of ions, then the charge in the substance due to this process is $-y$. We thus have the following distribution of charges :

(1) x in the apparatus, (2) $-x - y$ in the substance, (3) y in the medium.

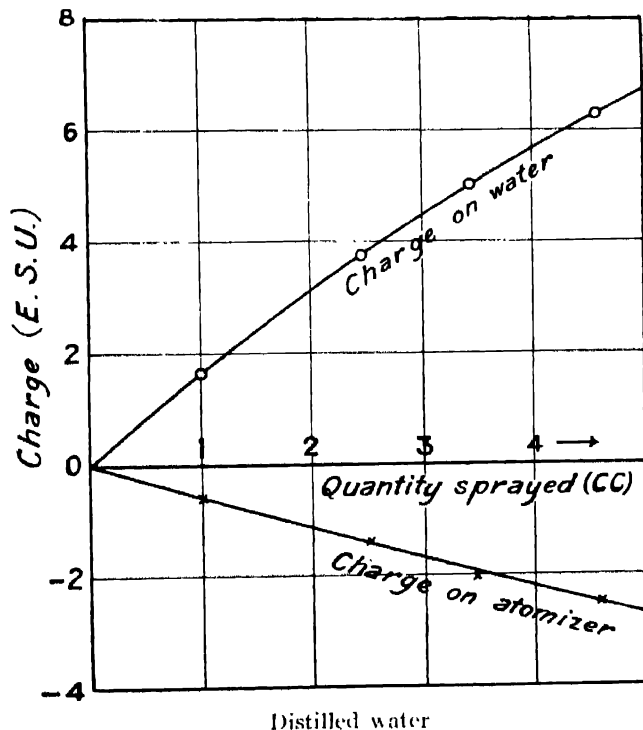


FIGURE 2

If initially the substance as well as the medium are uncharged, we should expect the algebraic sum of the total charge developed in the apparatus, in the substance and the medium to be equal to zero in any mechanical process of this kind. In any single experiment it is, however, not easy to prove this law quantitatively. For it is an extremely difficult matter to collect all the charges developed and measure them accurately. We can illustrate this by reference to a simple experiment. If distilled water is sprayed (by a De Vilbiss Atomizer No 15) the charges in the sprayer and the receiver are found to vary as shown in Fig. 2. The charge developed per c.c. of water sprayed is approximately as indicated below :

In the water = $+1.7$ e.s.u.

In the sprayer = -0.5 e.s.u.

In air = -1.1 e.s.u.

Within the limit of experimental error, therefore, the total charge is zero. The negative charge is slightly less than the positive charge. This may be partly due to the fact that all the ions are not caught by the Ebert's apparatus. The actual magnitude of the charge also varies widely according to the process employed. Thus 1 c.c. of water striking a plate gets a charge of 0.234 e.s.u., while 1 c.c. of water broken in a vertical blast of air gets only 0.023 e.s.u. This difference is largely due to the difference in the intensity of mechanical action and, therefore, also to the differences in the amounts of new surface developed in the two processes. A jet striking a plate breaks into a large number of small drops, while a drop broken in a vertical blast of air is broken into two or three drops only, so that in the former case the new surface developed is considerably more than that in the latter. Furthermore, the surfaces in action when drops strike against a metal plate are different from those in action when drops break in the air. In the former case besides water and air a metal plate is involved.

5. RELATIONSHIP BETWEEN WORK DONE AND CHARGE PRODUCED

The charge in the substance is equal and opposite to the sum total of the charges in the apparatus and the medium.

The whole of the work done in producing mechanical action is not utilised in the generation of charge. A part of it is utilised in producing motion and mechanical disruption and another part in working against friction, or, in other words, in the generation of heat. If the total work done is W , and if that part of it which is utilised in producing motion, mechanical disruption, and production of heat be W_0 , then $W - W_0$ is the work done in producing electric charge. If Q is the charge developed in the substance, then clearly

$$W - W_0 = AQ^2,$$

where A is a constant, which is dependent on the substance used and the mechanical process employed.

While it is comparatively easy to determine W , it is not always easy to determine W_0 . It is not, therefore, always possible to obtain quantitative relationships and we have in many cases to remain satisfied with the qualitative law, which is well recognised, that the charge in the substance, as well as the number of ions of either sign in the medium, which are developed in the mechanical process, depend on the intensity of the mechanical operation.

How the charge developed in the substance increases with the violence of the mechanical action can be illustrated by a simple experiment. If we have a single downward jet striking an insulated plate, the work done can be varied by altering the head of water in the tube. The results obtained in an experiment of this kind are given in table I. The jet was produced by a tube having a narrow orifice of diameter 0.2 mm. The pressure head in the tube was varied and the orifice was placed at a height of about 8 cm. above the bottom of the receiver.

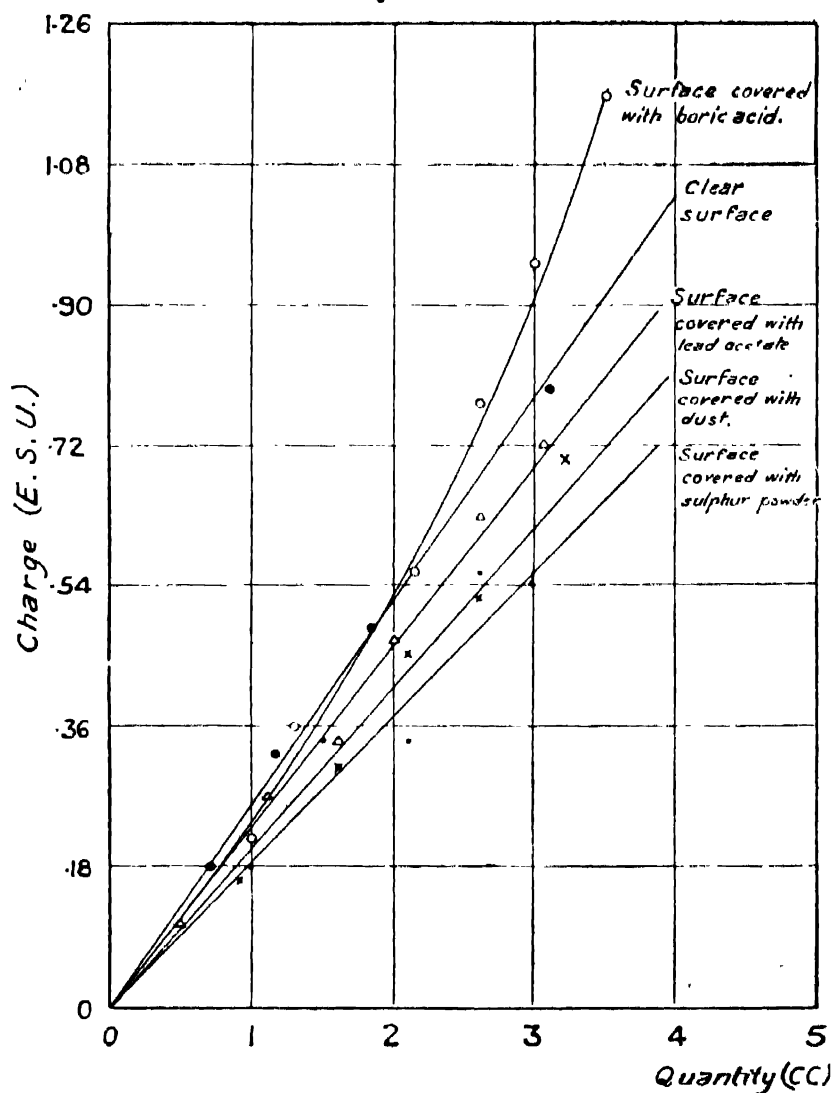
TABLE I

Distilled water (single jet)

Pressure head above the orifice in cm. of water	Kinetic energy per c.c. at the instant of break in c.g.s. units (approx.).	Charge per c.c. in c. s. u.
42	49,050	0.12
56.5	63,275	0.15
59	65,725	0.18
66	72,595	0.22
75	81,425	0.29
83	89,270	0.37
92.5	98,590	0.41
102	1,07,910	0.59

The experiment shows roughly that when the energy at the instant of break was doubled, the charge produced increased about four times. The charge

produced depends also to a certain extent on the nature of the surface on which the jet falls. This will be clear from Fig. 3.



Jet of distilled water falling on clear receiver and on surface covered with different substances

FIGURE 3

Similarly when two jets strike against each other, the charge produced depends not only on the height of the liquid columns but also on the diameter of the jet. With two jets produced by liquid columns each 70 cm. high, the following figures were obtained :

TABLE II

Distilled water (two jets striking at angles between 22° to 25° and placed about 8 cm. above receiver)

Diameter of jets in mm.	Average radius of drops produced. cm.	Average volume (c. c.) of drops produced.	Charge per c. c. in e. s. u.	Charge per drop in e. s. u.
0.2 } 0.2 } 0.33 }	3.4×10^{-2}	0.000164	0.110	1.8×10^{-5}
0.33 } 0.50 }	4.5×10^{-2}	0.000370	0.073	2.8×10^{-5}
0.48 }	8.5×10^{-2}	0.002556	0.060	1.53×10^{-5}

With increase in the diameter of the bores the size of drops produced is increased and, consequently, there is a decrease in the charge produced.

Table III gives the charge obtained in the substance as well as in the medium when 1 c.c. of water is subjected to the processes indicated therein.

TABLE III

Distilled Water

Process.	Charge derived from 1 c.c. of water.				
	Charge in substance e. s. u.	Charge in air (ions).			
		Positive e. s. u.	Negative e. s. u.	Total e. s. u.	Ratio : $\frac{\text{Pos.}}{\text{Neg.}}$
(1) Air bubbling through water.	+ 0.010 (about)	0.0003 (about)	0.0050 (about)	- 0.0047 (about)	1 : 15
(2) Drops broken in a vertical blast of air (Simpson).	+ 0.023	0.0046	0.0138	- 0.0092	1 : 3
(3) Two jets of water striking against each other.	+ 0.140	0.005	0.064	- 0.060	1 : 12
(4) A single jet striking a plate.	+ 0.234	0.008	0.095	- 0.087	1 : 12
(5) Water sprayed.	+ 1.70	1.00 } 0.84 } 0.85 }	0.89 } 1.97 } 1.69 }	- 1.00	1 : 2.1 *

* This ratio decreases to 1 : 1.6, if the rate at which a given quantity of water is sprayed is increased.

Table IV gives a comparison of charge developed in other substances.

TABLE IV

Charge in substance per c.c. in c.s.u.

Substance.	Two jets striking.	Single jet striking receiver.	Spraying.
Turpentine	...	-0.14	-0.54
Petrol	-0.015	...	-0.07
Ether	+0.56	+0.63	+1.68
HCl 3.65 gm /litre	-0.16	-0.26	-0.31

The charge developed per c.c. is greater when a substance is sprayed than when a jet strikes the receiver; also it is greater when drops are broken by a jet striking a receiver than by two jets striking against each other.

6. THE ELECTRICAL DOUBLE-LAYER

If we assume the existence of a double-layer, the positive charges, in the case of a water drop in contact with air will, according to the usual conception, be situated upon the molecules of water, and the negative charges upon those of the medium, *i.e.*, air. Such a double-layer is illustrated in Fig. 4. When the two layers are next to each other, the drop as a whole shows no charge. If there is a slip in the double-layer due to friction or other causes, the drop acquires a positive charge and the medium a negative charge. On the other hand, air bubbling through water gets negatively charged, for precisely the same reason, namely, the slipping of the double layer.



FIGURE 4

From the fact that when this drop is broken, we get ions of both signs in the air, we can immediately conclude that ions come out from *both* the layers. Moreover, from the fact that the negative ions are always in excess of the positive ions, we can conclude that ions come out more easily from the outer layer than from the inner layer.

When water or any other liquid comes through a metal tube, such as the tube of the atomizer or a jet, how does the tube get charged? We must assume an electrical double-layer to exist at the interface between the liquid and the metal tube. The moving liquid may produce a slip in the layer, and thus make the tube and the liquid get equal and opposite charges. There is also the "collector" action. Just as in a Kelvin water-dropper, the issuing drops in an electric field make the vessel get a charge opposite to those of drops, so also when liquid comes out through a metal tube, the tube must get a charge opposite to that of the drops if there is a pre-existing electric field, or the charges in the drops create such a field.

It is not easy to describe in simple language as to which of the processes mentioned in table III is more violent. When air bubbles through water, it is more or less a case of slipping; so that we get in the air ions from the layer adjoining the air surface, that is to say, negative ions. When two jets of water strike against each other in the air, the process is slightly more violent. But in this case three factors contribute to the production of charge both in the substance and in the air. In the first place, the slipping of the double layer which occurs when water moves through the tubes makes the water jets positively charged. Secondly, when the jets break in the air into drops, they acquire further positive charge and give the excess negative charge to the air. Finally, when the drops strike against the receiver, the positive charge is further augmented, the excess of negative charge being given to the air. When drops are broken in a vertical blast of air, all the above three factors contribute to the production of charge. There is, however, the following difference in the two cases:—

(1) The slipping of the double-layer during movement through the tubes gives to the water jets much greater positive charge than to the drops which come out slowly one after another.

(2) The drops formed per c.c. are slightly more in number when two jets strike against one another than when drops are broken in a vertical blast of air. In the former case, action is between water and water and in the latter, between air current and water. The result is that in the former case, both the substance and the medium (as determined by total of positive and negative ions) receive greater charge, but in the latter the air current dislodges a greater proportion of positive ions so that the ratio of positive to negative ions is greater in the latter than in the former case.

When a jet is directed against a receiver, the action is more violent than when two jets strike against each other with the result that the charges developed both in the substance and the medium are very much greater ; the ratio of the positive to negative ions is, however, very nearly the same in the two cases. With an atomizer the process is very violent and ions are dislodged from both the layers and there is only a very slight excess of negative ions.

The fact that in these experiments, there is always an excess of negative ions suggests that there is one layer from which ions are more easily removed than from the other. This clearly must be the layer or the charges situated upon the molecules of the medium, that is to say, the air in this case.

In the case of the substances given in table V, the number of positive and negative ions in the air are found to be very nearly equal, and the substances to develop very little charge. The data regarding charge in the air given in the table are those obtained by Eve converted into electrostatic units. These results were generally confirmed by independent experiments.

TABLE V
(Sprayed by atomizer)

Substance,	Charge derived from 1 c.c. of substance.		
	Charge in the substance. e.s.u.	Charge in the air (e. s. u.).	
		Positive.	Negative.
Amyl alcohol	Negligible	3·8	3·8
Acetone	"	2·0	2·0
Methyl alcohol	"	3·4	3·4
Ethyl alcohol	"	3·9	3·9

Such substances as amyl acetate, chloroform, aldehyde, acetic acid, also give equal number of positive and negative ions in the air on being sprayed, and acquire very little charge themselves.

If there are equal numbers of positive and negative ions in the air, the substance and the apparatus either collectively or separately remain uncharged, however violent is the mechanical process to which the substance is subjected.

If the double layer be supposed to exist in these cases it is clear that the medium must have derived ions from both the layers with equal ease. The inside layer in these cases is not more firmly adhering than the outside layer.

Substances generally get positively or negatively charged according as there is an excess of negative or positive ions in the air.

This result is true only in those cases where the charge acquired by the apparatus is small compared with the charge in the substance and in the air. This result was firmly established in the case of water in Simpson's experiments. In the qualitative experiments of Rudge, he came across some contradictory results showing that the substance and the medium had charge of the same sign. On careful scrutiny of his experiments, it appears that when dust is blown, or allowed to rain through a sieve, the blower or the sieve as the case may be, gets charged. The charges in the dust particles, in the air, and in the blower (or sieve) are equal to zero collectively. In those cases where the number of ions of both signs in the medium is very small or where the number of ions of one sign is very nearly equal to the number of ions of the other sign, often contradictory results are recorded in the sense that the substance is sometimes found to be positively charged and sometimes negatively charged. These appear to be due to errors in the experiments. Even the same chemical taken from two different bottles gives different results on account of slight differences in the impurities. Unless the samples are taken from the same source and the apparatus is carefully protected from stray electrification by earthed covers, and also sources (sources of ionisation) which might produce such electrification are carefully eliminated, these experiments often prove to be very elusive.

In the case of substances given in table VI the charge in the substance is of opposite sign to that of the resultant charge in the medium, except for turpentine and acetylene tetrachloride.

TABLE VI
(Sprayed by atomizer)

Substance.	Charge derived from 1 c.c. of the substance in e.s.u.			
	Charge in the substance.	Charge in air.		
		Posi	Negative.	Resultant.
Ether	+1.68	3.15	4.25	-1.10
Toluene	+0.2	0.01	0.05	-0.04
Carbon disulphide	+0.02	0.04	0.05	-0.01
Ammonia liquid (concentrated)	+1.2	1.35	2.01	-0.65
Benzene	-0.09	0.06	0.12	-0.06
Turpentine	-0.54	0.12	0.33	-0.21
Acetylene tetrachloride	-0.47	1.67	2.62	-0.95

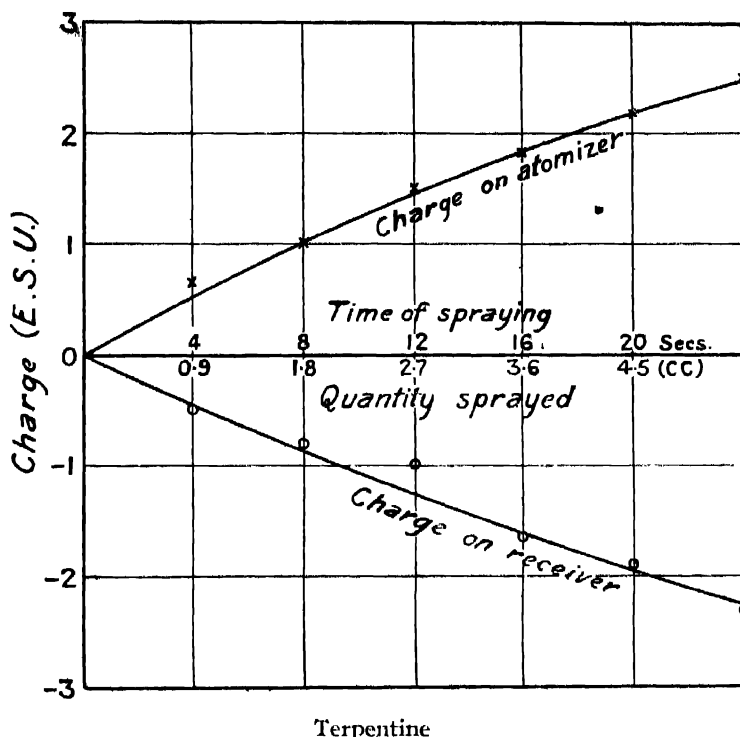


FIGURE 5

In the case of turpentine and acetylene tetrachloride the charges in the substance and that in the medium are of the same sign, because the charge developed during movement through the tube of the atomizer is large compared with that developed in the breaking process. This is clearly seen from Fig. 5, which gives the charge developed in the apparatus and the substance when different quantities of turpentine are sprayed. The charge (x) of the apparatus is positive and greater than the charge ($-x-y$) of the substance. y is negative and has a smaller value than x .

7 SOLUTIONS

When distilled water is sprayed it gets positively charged, but when a small quantity of common salt is dissolved in it, it gets negatively charged. It is, therefore, of interest to consider how the positive charge changes to negative as the concentration of the dissolved substance is increased. The measurement of charge in a salt solution, when a jet strikes a plate was originally made by Lenard. Subsequently, Busse measured the number of ions in the air obtained with salt solution jets, but, unfortunately, did not record the charge in the substance. The experiment was, therefore, repeated. Table VII gives the charge in the substance, in the apparatus and the medium when a jet of a solution

of NaCl of different concentrations is made to strike the receiver. The experiment is a difficult one, and the values of the charge in the air, particularly the low values, are to be considered as rough estimates. The results are in general agreement with those of Lenard and Busse.

TABLE VII

Single jet : head of water 70 cm. ; jet 8 cm. above receiver

NaCl dissolved in water : Concentration.	Charge derived from 1 c.c. of substance (c.s.u.).					
	In substance	In apparatus.	In air.*			
			Positive.	Negative.	Resultant.	Ratio : $\frac{\text{Neg}}{\text{Pos.}}$
0 (Distilled water)	+0.234	-0.13	0.008	0.095	-0.087	11
0.005%	-0.288	+0.25	0.003	0.010	-0.016	6.7
0.01%	-0.310	+0.28	0.002	0.013	-0.011	6.6
0.1%	-0.293	+0.27	0.001	0.003	-0.002	3.0
1.0%	-0.210	+0.20	0.0005	0.007	-0.0002	1.4
3.0%	-0.220	+0.23	0.003	0.001	+0.002	0.3

* Busse gave the following relative values for the total charge of positive and negative ions in air :—

Concentration % of salt solution.	-ve ions.	+ve ions.
0	540	40
0.005	100	15
0.01	66	10
0.1	15	5
1.0	5	3.5
3.0	4	6
5.5	3.5	6.1
9.0	3	5.0
16.0	2	4.3

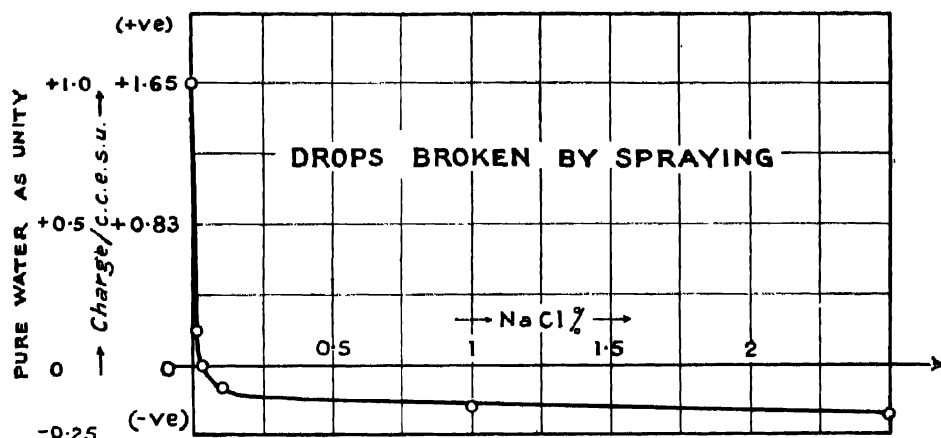


FIG. 6.

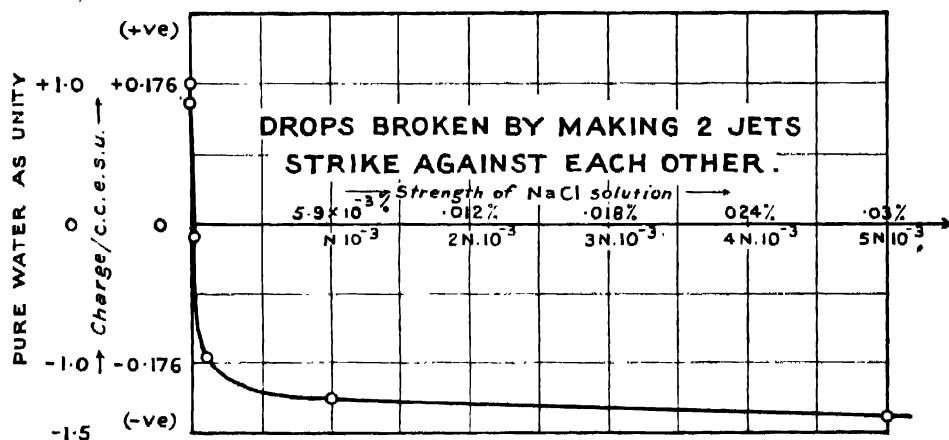


FIG 7

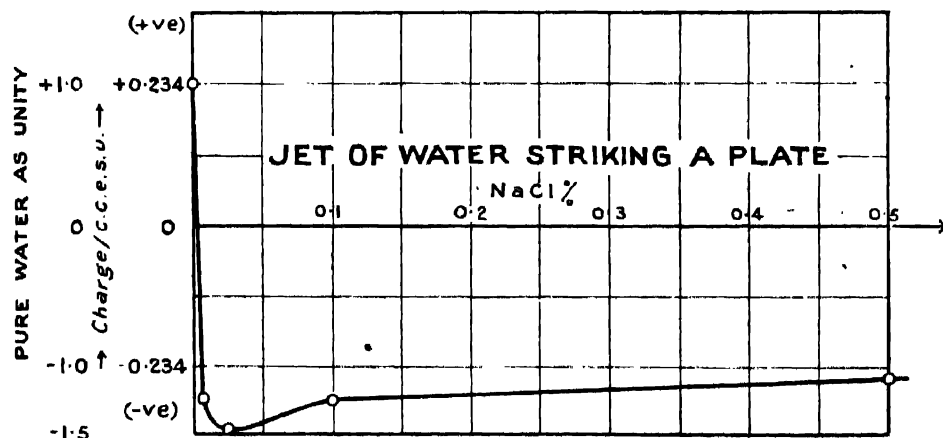


FIGURE 8.

It will be observed that the charge developed on drops changes very sharply from positive to negative, the particular concentration at which the transition

from positive to negative charge takes place depends on the violence of the process of breaking drops. This will be clear on comparing Figs. 6, 7, 8, which give the charge in the substance when solutions of NaCl of different concentration are broken into drops by the following processes :—

- (i) By spraying. (ii) By making two jets strike against each other.
(iii) By making a jet strike a plate.

Spraying by an atomizer is the most violent of the breaking processes, and transition from positive to negative charge on the liquid takes place at a concentration of about 0.025 per cent. Next to this in violence comes a single jet striking a receiver and in this case transition from positive to negative takes place at a concentration of about 0.002 per cent. Breaking of drops by making one jet strike against another is a comparatively weak process. In this case transition from positive to negative takes place at a concentration of about 5×10^{-5} per cent. There is apparently a reversal of the double-layer when NaCl is dissolved in water. A milder mechanical action removes considerably more positive ions than negative into the medium and thus changes the charge of the solution from positive to negative at a lower concentration than stronger mechanical action.

It will be observed from the figures given in table VII, that while the charge in the substance changes from positive to negative at a concentration of about 0.002%, the charge in the medium continues to remain negative even when the concentration reaches 1%. This is not easy to explain in view of the fact that the charge in the tube is positive and only slightly less than or very nearly equal to the charge in the substance for all concentrations from 0.005% to 1%. The solution came out of the tube with a negative charge and this charge did not appreciably increase or decrease as a result of impact with the plate. The excess negative charge in the air may have been due to fine spray from the negatively charged solution. The resultant charge as well as the ratio of negative to positive ions, however, progressively decreased as the concentration was increased to 1%. At a concentration of slightly more than 1%, the number of positive and negative ions in the air was equal. When the concentration was still further increased, the number of positive ions became very slightly greater than the number of negative ions.

When a jet of dilute hydrochloric acid is broken into drops, the charge developed on the drops similarly changes from positive to negative at a certain concentration. The figures obtained in one experiment are given below:—

Dilution.	Charge (e.s.u.).
HCl 0.00012 gm./litre	+ 0.182
" 0.00023 "	+ 0.094
" 0.0023 "	- 0.187
" 0.0092 "	- 0.239
" 0.023 "	- 0.254
" 0.046 "	- 0.254

How does the reversal of the double layer take place when NaCl is added to distilled water ? Is this associated with a concentration of Na^+ and Cl^- at the surface ? This point is discussed in § 12 *et seq.*

8. SOLID PARTICLES

The case of solids has received investigation in a large number of papers by Shaw¹⁰ on tribo-electricity. He shows that when two identical solids, whether of ebonite, or celluloid, or silk, are rubbed together, each becomes charged in a systematic way. The charges are attributed by him to differential strain on the surfaces, caused by the rubbing. Experiments made by him in vacuum give results similar to those in open air; he, therefore, concludes that the results are entirely due to changes on the solid surfaces; and not, even in part, to the action of films on solid surfaces.

An effect which simulates strain; in as much as the tribo-electric state of a solid surface is changed by the process of rubbing it with a fabric, is shown by Shaw to be due to the deposition on the surface of organic films derived from the fabric. These recall the "primary" films used by Sir Wm. Hardy in researches on boundary lubrication.

It has been known that dissimilar materials when struck together in normal impact develop opposite charges.¹¹ But Shaw on trial found that identical bodies also charge one another. A glancing blow, containing tangential as well as normal stresses, is best for the purpose. The result of a violent blow between identical specimens of insulating materials is to give a net negative charge almost invariably, whether the surfaces be standard or strained. Prolonged blows in general increase the net negative charge.

The following results were obtained by the writer with solid particles (1) issuing as a jet through an orifice of 3 mm. and striking a receiver placed 12 cm. below, and (2) in the form of two streams moving on plains inclined at about 100° and striking against each other in the air.

TABLE VIII

Substance	Weight in gm. per c c. of loose powder	Single jet charge/gm. e.s.u.	Two streams striking charge/gm. e.s.u.
Aluminium (filings)	1.17	0.039	0.054
Brass (filings)	1.69	-0.034	-0.336
Iron (filings)	2.39	-0.252	-0.250
Dust	1.3	-0.014	-3.200
Sulphur	1.06	-3.998	-6.719
Chalk	0.58	0.414	9.180
Boric acid	0.42	-2.088	-14.558
Lead acetate	1.48	0.190	1.429

The results are in general agreement with Shaw's observations. The impact in the air very greatly augments the charge obtained by merely making a jet strike a receiver.

These data may be compared with Rudge's results (qualitative) as given in table IX.

TABLE IX

Material.	Sign of charge.	
	Substance allowed to rain and fall on a receiver.	Substance being sprayed.
Silica	Negative	Positive
Mercury sulphide	"	"
Red lead	Very slight negative ; sometimes positive	Negative
Precipitated sulphur	Negative but not strong	Positive
Iron filings	Negative	Negative
Chalk	Very slight positive but tending to become negative	"
Zinc dust	Negative	"
Thorpic	"	"
Cornflour	"	Positive
Ground crystallised sulphur	"	"

These observations show that when solid particles strike against each other the charge they acquire is often different in sign from that acquired by them mainly by friction through air, namely, when they are sprayed, except in the case of metals.

PART III—SUBSTANCES INITIALLY CHARGED

9. EXPERIMENTAL DATA

In order to determine the precise constitution of the double-layer, experiments were also carried out with substances which were given initially a charge. These show that during the process of breaking of drops, the initial charge remains in the drops. Each of the broken drops has a charge which is equal to its initial charge *plus* the charge which it would get as a result of breaking if it had no initial charge. Any exchange of electric charge that takes place between the substance and the medium is derived entirely from the double-layer, if such a layer is supposed to exist. The initial charge, if any, remains in the substance ; it is not dislodged by the process of breaking.

The data for water are given in table X.

TABLE X
Distilled water—initially charged

Initial potential (positive or negative) Volts.		Charge in substance per c.c. (e.s.u.).			Charge in air per c.c. of water (e.s.u.).					
		For positive initial potential.		For negative initial potential.	Mean of 2 and 3.		For positive initial potential.		For negative initial potential.	
		2	3	4	5	6	7	8	9	10
		Positive ions.	Negative ions.	Resultant charge.	Positive ions.	Negative ions.	Resultant charge.	Positive ions.	Negative ions.	Resultant charge.
(a) Water sprayed.										
1	—	—	—	1.58	+0.78	-1.56	-0.78	+0.78	-1.56	-0.78
2	+2.26	+0.75	—	1.51	—	—	—	—	—	—
4	+3.08	0	—	1.54	+0.72	-1.32	-0.60	+0.70	-1.50	-0.80
10	+5.00	-1.87	—	1.57	+0.60	-1.46	-0.86	+0.68	-1.36	-0.68
20	+9.46	-6.14	—	1.66	—	—	—	—	—	—
30	+12.84	-9.78	—	1.53	—	—	—	—	—	—
(b) Single jet.										
0	—	—	—	0.259	0.008	-0.098	-0.090	+0.008	-0.098	-0.090
2	+1.847	-1.283	—	0.282	0.007	-0.086	-0.080	+0.008	-0.092	-0.084
4	+3.490	-2.934	—	0.278	—	—	—	—	—	—
10	+7.867	-7.398	—	0.235	—	—	—	—	—	—

It is clear from columns 2, 3 and 4 of the above table that if Q_0 be the charge acquired by 1 c.c. of water, initially uncharged, when it is broken into drops by some mechanical process, then the same quantity of water when given an initial charge of $+Q_0$ or $-Q_0$ units of electricity, and broken into drops in the same manner, will acquire charge of $Q_0 + Q_0$ or $Q_0 - Q_0$, according as the initial charge is $+Q_0$ or $-Q_0$. This means that the initial charge of the liquid has no effect on the amount of electricity which is developed when it is broken into drops by any mechanical process. This is also confirmed by the amount of electricity in the air given in columns 5 to 10 of the above table, which remains very nearly the same whatever be the initial charge of the water.

Similar results are obtained with other liquids. Table XI gives the results obtained with acetylene tetrachloride and bromoform :—

TABLE XI

Potential of sprayer. Volts.	Charge per c.c. of acetylene tetrachloride. (e s.u.)			Charge per c.c. of bromoform. (e s.u.)		
	For positive initial poten- tial.	For negative initial poten- tial.	Mean of 2 & 3	For positive initial po- tential.	For negative initial po- tential.	Mean of 5 & 6.
1	2	3	4	5	6	7
0	—	—	-0.05	—	—	-2.36
2	-0.126	-1.287	-0.66	—	—	—
4	+0.536	-1.854	-0.66	-0.61	-3.70	-2.17
10	+2.808	-3.168	-0.68	—	—	—
20	+4.482	-5.901	-0.71	4.16	-8.71	-2.27
30	—	—	—	5.85	-10.95	-2.05

10 GAS JETS

Charging by a gas jet, such as escaping steam or carbon dioxide, is fairly well-known. The point of very great interest, however, is that some gas will charge the nozzle through which it escapes or the plate on which it impinges positively, while others will charge it negatively. The charge developed when a jet of gas is made to impinge on a plate depends on the nature of the gas, its pressure, the diameter of the nozzle, and the distance of the plate from the nozzle. For instance, in one experiment, carbon dioxide, issuing from a cylinder containing liquid carbon dioxide (at about 70 atmospheres) through a

nozzle 2 mm. in diameter and striking a plate placed at a distance of 6 cm. from the nozzle, gave the following charge on the plate :—

	Charge (e.s.u.).
In the 1st second	-0'36
In 2 seconds	-0'72
In 3 seconds	-1'44
In 4 seconds	-2'70
In 5 seconds	-3'60

There was vigorous ionisation, and the usual leak of 1 per cent. per minute of the electrometer increased to about 4 per cent. per minute in the first few minutes. The magnitude of charge decreases very rapidly with decrease of pressure and a jet issuing under very low pressure (two or three atmospheres) gives very little charge.

Acetylene, on the other hand, gave positive charge on the plate. This gas issuing under a pressure of about 18 atmospheres through a nozzle, 1 mm. in diameter, and striking a plate placed at a distance of 4 cm. would charge the plate at a rate of 0'09 e.s.u./second. In this case also there is vigorous ionisation and the usual leak of about 1 per cent. per minute of the electrometer was found to increase to about 8 per cent. per minute in the first few minutes.

Is the charging produced by an escaping gas due to the impinging of solid particles? In the case of escaping steam, we have the water drops impinging on the walls of the nozzle. The CO_2 comes out from a cylinder of liquid carbon dioxide probably as solid particles. Acetylene gas is not usually compressed into cylinders but is dissolved in acetone, with which the porous mass inside the cylinder is impregnated, and, therefore, when it escapes, it probably carries with it a fine spray of the liquid. We have, however, the following statement by C.T.R. Wilson¹² :—"According to a large class of theories the air in contact with the ground acquires a positive charge, *i.e.*, by friction." Are we to assume that there is a double-layer between air and earth's surface, and that the movement of air causes a slip, there being no appreciable separation of charge unless the velocity is great?

If we assume that there is an electrical double-layer in operation, it cannot be that the outer charge of the normal double-layer between the plate and air is removed by the impinging gas, for in that case the plate would show charge of the same sign both in the case of carbon dioxide and acetylene. Can the development be explained by the following two processes :—

(1) At the nozzle, there is a double-layer between the gas and the metal surface of the nozzle, and the frictional action on this double layer gives the issuing gas a charge.

(2) When this charged gas impinges on the plate a similar double-layer is instantly formed between the gas and the plate, and friction accentuates the charge on the already charged gas.

II. MECHANICAL ACTION IN THE ATMOSPHERE

In the atmosphere we get numerous examples of generation of charge by mechanical action. Over the sea surface, the splashing of sea water makes the water negatively charged and this undoubtedly plays a very important rôle in the replenishment of the earth's negative charge. In thunderstorms, we have examples of water drops striking against each other or being broken in a vertical blast of air. There are also the ice particles striking against each other and getting negatively charged in the higher region of the clouds. The generation and distribution of charge in thunderclouds are subjects which have received elaborate investigation in recent years. In sandstorms and snowstorms (blizzards) we have other examples of generation of charge by mechanical action. Fog particles probably get charged by condensation on ions or charged nuclei or by a slip of the double-layer during movements through air.

It is essential to realise an important distinction between the processes in operation in the atmosphere and those in the laboratory. In the laboratory we are unable to generate charge without making use of some sort of apparatus, and the reaction between the apparatus and the liquid or solid particles always makes the drops or the solid particles leave the apparatus with an initial charge. Earthing the apparatus makes no difference; while the charge in the apparatus escapes into the earth, the drops or the solid particles leave it with an equal and opposite charge. In these experiments the total charge is shared between the apparatus, substance, and the medium. The initial charge profoundly affects the relationship between the charge in the substance and that in the air, and we sometimes find that they are of the same sign. For instance, when a solution of NaCl is broken by spraying or by making a jet strike a plate, the charges in the substance and the air are of the same sign for the range of concentration 0.005% to 1%. When drops are broken in a vertical blast of air, they come out of the tube with an initial charge, with the result that while the drops after being broken by the air current get a charge of +0.023 c. s. u./c.c.) the total charge in the air is less than half this amount. In the atmosphere, there is no apparatus; the drops may form on ions or nuclei, and may have an initial positive or negative charge, but if they are broken in a current of air, the total charge in the air which will be derived from 1 c.c.

will be roughly -0.0092 e.s.u. and the charge acquired by the drops by this operation will also be equal to this amount but positive in sign. This *plus* the initial charge will determine the total charge of the drops. If the drops break by striking against each other, the charge in the air will be roughly -0.060 e. s. u./c.c. and in the drops the initial charge $+0.060$ e. s. u. per c.c.

We may give here one example showing how the calculation of charge in atmospheric processes is modified when we take these aspects into consideration. As explained in a previous paragraph, with increasing amounts of dissolved salts (NaCl) or acids (HCl) in distilled water, the charge developed on drops changes very sharply from positive to negative. It also appears from these experiments that when drops are broken by a comparatively mild process, such as, by making one jet strike against another or in a vertical blast of air, the transition from positive to negative takes place at a very low concentration, roughly of the order of 5×10^{-5} per cent.

Now, it is known that when evaporated to dryness, 100,000 parts by weight of rain water will give about 0.34 part of solid matter and that most of this consists of sodium chloride and organic matter. This is equivalent to a concentration of 3.4×10^{-3} per cent. Near sea coast and towns the impurities are usually more than this amount. As the impurities are collected during the journey through air, the contamination may be regarded to be slightly less than this amount in the region where drops are first formed; also the rain which falls at the end of a shower is less contaminated than that which falls at the beginning. We shall, therefore, not be far out if we assume that the concentration of chlorides in rain drops is always greater than 10^{-4} per cent. except towards the end of a shower. If, therefore, charge is developed in a thundercloud by breaking of drops or by drops striking against each other, and if the salt content of rain drops be as much as the average value (0.0034%) or more, the charge developed is either very small positive or negative. We are so near the transition point that we can develop very little charge by breaking of drops. It is only when the drops have very little contamination that we can develop a large quantity of positive charge by breaking them. Simpson's calculation of sparking potential in clouds produced by the breaking process would, therefore, seem to need a revision. It is also probably due to this reason that the breaking process is no longer found to play the same important part in the generation of charge in thunderclouds as it was once supposed to do.

12. HOW IS CHARGE DEVELOPED?

We now proceed to consider the different factors which may contribute, to the generation of charge in the various processes employed.

We know that when crystals are split, charges¹³ are found, for instance in calcite, selenite, mica, fluor spar, gypsum, etc. Is the charge developed by

strain, disruption, cleavage, deformation, etc., a pure consequence of removal of electrons from or addition of electrons to the two surfaces by the forces in operation ? As has been already pointed out by Shaw, the following factors come into consideration in this connection :—

(1) The contact effects¹⁴ somewhat akin to the Peltier P.D. between metals.

(2) The rôle of absorbed films.¹⁵ According to Nernst's theory the metals go into solution when brought into contact with liquid films, each metal having its own solution pressure and receiving a corresponding greater or less negative charge. Coehn supposes that even insulators like glass are merely bad electrolytes, so that even for these solid contacts the Nernst principle holds good. When a liquid rubs a solid we should have the electrokinetic phenomenon of "stream potential," the converse of electro-osmose, whereby the solid would be charged according to Helmholtz's formula. It has been shown by various writers, notably Knoblauch, that an acid surface has itself a negative, and an alkaline one a positive tendency. In the first case the surface loses $+(H)$ ions in the latter $-(OH)$ ions. As surfaces are commonly acidic or alkaline, this must be an important factor in the generation of charge.

(3) According to the electron theory of matter the interface P.D. varies as the absolute temperature, and, consequently, the temperature changes caused by friction, disruption, fusion, evaporation, etc., must contribute to the production of charge.

(4) The physical changes in the surfaces as a result of rubbing, etc., and their relationship to the tribo-electric properties constitute another very important factor according to Shaw.

Therefore, the net potential V can be expressed as

$$V = E - P \pm S - M \pm A - T,$$

where

E = electron surrender causing a P.D. akin to the Peltier P.D.,

P = solution pressures (Nernst),

S = strain effect (Shaw),

M = moisture effect (French, Vieweg),

A = acid effect (positive) $\left. \begin{array}{l} \\ \text{alkaline effect (negative)} \end{array} \right\} \text{ (Knoblauch),}$

T = effect due to temperature changes at the interface.

In any specific case, one or the other factor may be absent, and some factors may become more important than the others.

Coming to the question of electrical double-layer, Frenkel¹⁶ in a very interesting paper on the surface electrical double-layer of solid and liquid bodies showed mathematically that if the atoms be assumed to consist of positive nuclei with electrons rotating about them, these electrons constitute over the surface of the metals a layer of negative electrification with a corresponding layer of positive electrification on the inner side of the surface, the electric double-layer of atomic thickness thus formed, preventing the free electrons from escaping. If, in the

same way, a double-layer is supposed to be formed on the surface of any solid, liquid or gas, then at an inter-face between two dissimilar substances, the charge on either face will be the net result of the positive charge on its inner side *plus* the negative charge on the upper side of the other face. If, in any case, the net effect of the combination on each of the two faces in contact happens to be a zero charge then clearly there is no double-layer formation. This will be the case at the interface between two substances of the same material. This may explain why by breaking a liquid in its own vapour we can develop very little charge.

There is thus evidence regarding the formation of a double-layer on the surface of all uncharged substances. As regards charged substances, we have seen that, in the exchange of electricity between a liquid and the surrounding medium, when the former is broken into drops, the initial charge of the liquid does not come into play. The initial charge of the substance must, therefore, be considered to be adhering to it during the process of division. The double-layer, therefore, must be considered to be a natural formation at the boundary between two surfaces in contact, between solid and solid, solid and liquid, solid and gas, liquid and gas, etc., which remains inactive until there is a slipping or disruption ; it is formed whether the substances are initially charged or uncharged. It is purely a boundary phenomenon and all exchanges of electricity during the processes described, takes place from this boundary phenomenon. In any case, the assumption of the existence of an electrical double-layer enables us to explain the observed effects more easily than on any other assumption.

While we cannot say we understand yet fully how the charges are developed we must say that we have gained in recent years a good deal of insight into the processes in operation.

R E F E R E N C E S

- ¹ *Trans. Nat. Inst. Sci. India*, Vol. 1, No. 4 (1935). (*The Cataphoric Speed of Inorganic Colloids* by J. N. Mukherjee, S. G. Chaudhury and B. N. Ghosh.)
- ² *Ann. der Phys.*, **46**, 584 (1892).
- ³ *Phil. Mag.*, **37**, 341 (1894)
- ⁴ *Evc, Phil. Mag.*, **14** (1907).
- ⁵ *Ann. der Phys.*, **76**, 493 (1925)
- ⁶ *Proc. Roy. Soc., A*, **90**, 531 (1914).
- ⁷ *Phil. Mag.*, **25**, 481 (1913) ; *Proc. Roy. Soc., A*, **90**, 256 (1914).
- ⁸ *Proc. Roy. Soc.*, **39**, 243 (1927).
- ⁹ *Phil. Trans. Roy. Soc.*, **209A** (1909)
- ¹⁰ Shaw, *Proc. Roy. Soc., A*, **94** (1917) ; **118** (1928) ; **27** (1930) ; *Proc. Phys. Soc.*, **39** (1927)
- ¹¹ See Richards, *Phys. Rev.*, p. 295 (1920).
- ¹² Article on Atmospheric Electricity, *Dictionary of Applied Physics*, Vol. 3, p. 96
- ¹³ Vieweg, *Jour. Phys. Chem*, **30**, No. 7.
- ¹⁴ Fowler's *Statistical Mechanics* (Second Edition), pp. 352-64, 397-403.
- ¹⁵ Fowler's *Statistical Mechanics* (Second Edition), Chapter XIII, application to liquids and solutions, also p. 824, *et seq* discussing Langmuir's work on the subject
- ¹⁶ *Phil. Mag.*, **33**, 297 (1917).

DYNAMICS OF THE PIANOFORTE STRING AND THE HAMMER.—PART II (ELASTIC HAMMER)

By MOHINIMOHAN GHOSH

Burdwan Raj College (Bengal)

(Received for publication, Nov. 19, 1938.)

ABSTRACT. The dynamics of the pianoforte string and the elastic hammer has been worked out, following the operational method that was adopted in Part I. The elastic hammer is supposed to behave like a hard load backed by a weightless spring, while the string is considered as loaded, so long as the hammer remains in contact with it. Three different cases have been considered, according as the hammer strikes (i) very near the end (ii) at a finite distance from one end of a semi-infinite string (iii) at the mid-point. Of the three cases, only the first was considered by Bhargava-Ghosh, and afterwards the second case was considered by Das. Unlike the previous investigations on the subject, the present analysis does not require to assume Kaufmann's mass-correction.

INTRODUCTION

In Part I the dynamics of the damped pianoforte string and the hard hammer ¹ has been worked out by the help of *operational* method. In this paper we follow the same method for the elastic hammer, and retain the idea that the string behaves like a loaded string *so long as the hammer is in contact* with the string. Attempts were also made to study the above problem by Bhargava-Ghosh ² and Das ³. The former authors studied the case in which the elastic hammer strikes near the end of the string. Das afterwards tried to improve upon the analysis and also considered the case of hammer striking a semi-infinite string at a finite distance from one end. But these workers *substituted the effective mass of the hammer*, that was assumed by Kaufmann, *as such*, for the actual value of the same. The present analysis is, however, free from any such assumption and is perfectly general. Further, it includes the case of the finite string.

EXPLANATION OF THE SYMBOLS USED

- l = Length of the string = $a + b$.
- a = Shorter segment of the string.
- b = Longer segment of the string.
- t = Variable time.

x = Variable, measured along the length of the string;

The string is fixed at $x=0$ and $x=l$,

$x_1 = x - a$.

y = Displacement at any point of the string at a given time t ,

y_a = Displacement of the struck point, $x=a$,

y_1 = Displacement at any point, $x < a$,

y_2 = Displacement at any point, $x > a$.

ρ = Linear density of the string.

$M_1 = \rho a$ = Mass of the shorter segment of the string,

$M_2 = \rho b$ = Mass of the longer segment of string,

$M = \rho l$ = Mass of the string = $M_1 + M_2$,

m = Mass of the hammer.

c = Velocity of the transverse wave motion along the string

T = Tension along the string = $c^2 \rho$.

$\Theta = \frac{2l}{c}$ = Period of the free vibration of the string,

$$\theta_1 = \frac{2a}{c} = \Theta \frac{a}{l},$$

$$\theta_2 = \frac{2b}{c} = \Theta \frac{b}{l}.$$

$$t_n = t - n\theta_1,$$

v_o = Velocity of impact.

$$J = mv_o.$$

u = The compression of the hammer.

$z = y_a + u$ = Displacement of the hammer.

E = Elastic constant for the material of the hammer.

P = Pressure exerted by the hammer.

D = Operator $\frac{d}{dt}$.

The equation of motion of the string is

$$\frac{d^2 y}{dt^2} = c^2 \frac{d^2 y}{dx^2} \quad \dots (17)$$

which is equivalent to

$$\frac{d^2 y}{dx^2} = \frac{D^2}{c^2} y. \quad \dots (17.1)$$

The elastic hammer strikes at $x=a$, and if y_a is the displacement of the struck point, we get

$$y_1 = y_a \frac{\sinh Dx/c}{\sinh Da/c} \quad \dots \quad (18)$$

$$y_2 = y_a \frac{\sinh D(l-x)/c}{\sinh Db/c} \quad \dots \quad (18.1)$$

Following the assumption that was made in one of the previous papers,⁴ the elastic load is replaced by a hard load, backed by a weightless spring. The pressure P exerted by the load is given by

$$P = m \frac{d^2 z}{dt^2} = -Eu \text{ (By Hooke's law)} \quad \dots \quad (19)$$

and subsequent motion of the load is given by the equation (cf. eq. 2)

$$m \frac{d^2 z}{dt^2} = T \cdot \Delta \left(\frac{dy}{dx} \right)_{x=a} \quad \dots \quad (19.1)$$

where $z = y_a + u \quad \dots \quad (19.2)$

Now with the help of eqs. (19.2), (1.2) and (1.3), eqs. (19) and (19.1) can be written in the form

$$\left[mD^2 + D \frac{T}{c} \left(\coth \frac{Da}{c} + \coth \frac{Db}{c} \right) \right] y_a + mD^2 u = JD \quad \dots \quad (20)$$

and $mD^2 y_a + (mD^2 + E) u = JD \quad \dots \quad (20.1)$

Now solving the simultaneous eqs. (20) and (20.1) for y_a and u , we get

$$y_a = \frac{1}{F(D)} \cdot v_0 \quad \dots \quad (21)$$

$$u = (\coth Da/c + \coth Db/c) \frac{D}{F(D)} \cdot \frac{v_0 T}{Ec},$$

and from eq. (21), $u = \frac{T}{Ec} (\coth Da/c + \coth Db/c) Dy_a \quad \dots \quad (21.1)$

$$= \frac{T}{Ec} (\coth Da/c + \coth Db/c) y_a' \quad \dots \quad (21.2)$$

where $F(D) = D + \left(\frac{T}{Ec} D^2 + \frac{T}{mc} \right) \left(\coth \frac{Da}{c} + \coth \frac{Db}{c} \right) \quad \dots \quad (21.3)$

(i) When a is very small, i.e., the hammer strikes very near the end, b becomes large compared to a . We have, proceeding in the same way as is done to obtain (5), Part I,

$$y_a = \frac{Dv_0}{\frac{ap}{3} D^4 \left(\frac{1}{E} - \frac{a^2}{45mc^2} \right) + \frac{T}{Ec} D^3 + \left(1 + \frac{ap}{3m} + \frac{T}{Ea} \right) D^2 + \frac{T}{mc} D + \frac{T}{ma}}$$

As the coefficient of D^4 is small, it can be neglected, and we have, approximately,

$$y_a = \frac{Ev_0c}{T} \left[\frac{e^{at}}{(a-\mu)^2 + v^2} + \frac{e^{\mu t}}{v\sqrt{(a-\mu)^2 + v^2}} \right] \sin(vt - \epsilon) \quad \dots (23)$$

where a , $\mu + iv$ and $\mu - iv$ are the three roots of the cubic

$$\frac{T}{Ec} D^3 + \left(1 + \frac{ap}{3m} + \frac{T}{Ea} \right) D^2 + \frac{T}{mc} D + \frac{T}{ma} = 0 \quad \dots (24)$$

and are given by

$$\left. \begin{aligned} \mu &= -\frac{T}{2m_1c}, \\ v &= \sqrt{\frac{T}{m_1a} - \frac{T^2}{4m_1^2c^2}} = \sqrt{-\frac{2\mu c}{a} - \mu^2}, \\ a &= -\left(\frac{m_1}{m} \cdot \frac{Ec}{T} - \frac{c}{a} \right) = \left(\frac{E}{2m} \cdot \frac{1}{\mu} + \frac{c}{a} \right), \end{aligned} \right\} \dots (25)$$

$$\text{and } m_1 = m + \frac{ap}{3} + \frac{Tm}{Ea} = m_0 + \frac{Tm}{Ea},$$

$$\epsilon = \tan^{-1} \frac{v}{\mu - a};$$

when the load is hard, i.e., $E = \infty$, eq. (23) becomes same as that given by Kaufmann, for undamped string [vide Eq. (7), Pt. I].

Attempts were made to study a similar case by previous workers such as S. Bhargava and R. N. Ghosh² and also P. Das.³ Das attempted to make some improvement in the analysis given by previous workers. But even his treatment does not go without criticism. Das has assumed the corrected mass of the hammer due to Kaufmann as such and builds up his theory which when translated in the present notations should give an equation (vide eq. 6, of his paper³)

$$\frac{T}{Ec} D^3 + \left(1 + \frac{T}{Ea} \right) D^2 + \frac{T}{m_0c} D + \frac{T}{m_0a} = 0.$$

But the subsequent results obtained by Das are based upon the equation (*vide* eq. 8, of his paper ³)

$$\frac{T}{Ec} D^3 + \left(1 + \frac{T}{Ea} + \frac{\rho a}{3m_0} \frac{T}{E} \right) D^2 + \frac{T}{m_0 c} D + \frac{T}{m_0 a} = 0$$

which, however, does not follow from the preceding steps of his analysis.

The expression for y_a in eq. (23) is perfectly general and is *free from Kaufmann's assumption* for the mass correction used by Bhargava-Ghosh and Das. This equation, however, may be solved rigorously by following Cardan's well-known method.

From eq. (21.1) we get with the help of eq. (1.2) for this case,

$$Eu = \frac{T}{c} \left[\frac{D^2 a}{3c} + D + \frac{c}{a} \right] y_a \quad \dots (26.1)$$

$$= \frac{T}{c} \left(D + \frac{c}{a} \right) y_a, \text{ (neglecting the term containing } \frac{a}{3c} \text{ which}$$

is very small).

$$\dots (26.2)$$

Now, substituting the values of y_a from eq. (23), and after proper operation, we have, from eq. (26),

$$-P = Ev_0 \left[A_1 e^{at} + A_2 e^{\mu t} \sin(vt - \epsilon) + A_3 e^{\mu t} \cos(vt - \epsilon) \right] \quad \dots (27)$$

where, for eq. (26.1),

$$\left. \begin{aligned} A_1 &= \left(\frac{c}{a} + a + \frac{a^2}{3c} \right) / \left\{ (a - \mu)^2 + v^2 \right\} \\ A_2 &= \left\{ \frac{c}{a} + \mu + \frac{a}{3c} (\mu^2 - v^2) \right\} / v \sqrt{(a - \mu)^2 + v^2} \\ A_3 &= \left(1 + \frac{a}{3c} 2\mu \right) / \sqrt{(a - \mu)^2 + v^2} \end{aligned} \right\} \quad \dots (27.1)$$

and for eq. (26.2),

$$\left. \begin{aligned} A_1 &= \left(\frac{c}{a} + a \right) \cdot A_3^2, \quad A_2 = \left(\frac{c}{a} + \mu \right) A_3 / v, \\ A_3 &= 1 / \sqrt{(a - \mu)^2 + v^2} \end{aligned} \right\} \quad \dots (27.2)$$

ϵ , a , μ , and v are given in eq. (25).

Equations (27) represent the pressure exerted by the elastic load at different times, during impact.

Semi-infinite string :

(a) The elastic hammer strikes at a finite distance a , from the fixed end $x=0$ of the string, the other end $x=\tau$ being at a very large distance from the struck point, i.e., $b=\infty$.

From eq. (21.3)

$$\begin{aligned} F(D) &= D + \left(\frac{T}{Ec} D^2 + \frac{T}{mc} \right) \left(\coth \frac{Da}{c} + 1 \right) \\ &= D + \left(\frac{2T}{Ec} D^2 + \frac{2T}{mc} \right) \left(1 - e^{-D\theta_1} \right)^{-1} \quad \dots (28) \end{aligned}$$

$$\text{whence} \quad y_a = \frac{1 - e^{-D\theta_1}}{D_1 D_2} \left[1 - \frac{q+p}{D_1 D_2} e^{-D\theta_1} \right]^{-1} \quad \dots (29)$$

$$\text{where} \quad D_1 = D + q \quad \text{and} \quad D_2 = D + p \quad \dots (29.1)$$

and $-q$ and $-p$ are the roots of the equation

$$D^2 + \frac{Ec}{2T} D + \frac{E}{m} = 0,$$

and are given by

$$[q, p] = \frac{Ec}{4T} \mp \frac{1}{2} \sqrt{\left(\frac{Ec}{2T} \right)^2 - \frac{4E}{m}} \quad \dots (29.2)$$

From eq. (29),

$$\begin{aligned} y_a &= (q+p) \left[\frac{1}{D_1 D_2} + \left\{ \frac{(q+p)D}{D_1^2 D_2^2} - \frac{1}{D_1 D_2} \right\} e^{-D\theta_1} \right. \\ &\quad + \left\{ \frac{(q+p)^2 D^2}{D_1^3 D_2^3} - \frac{(q+p)D}{D_1^2 D_2^2} \right\} e^{-2D\theta_1} + \dots \\ &\quad \left. + \left\{ \frac{(q+p)^n D^n}{D_1^{n+1} D_2^{n+1}} - \frac{(q+p)^{n-1} D^{n-1}}{D_1^n D_2^n} \right\} e^{-nD\theta_1} \right] \quad \dots (29.3) \end{aligned}$$

$$= f_1(t) + f_2(t_1) - f_1(t_1) + f_3(t_2) - f_2(t_2),$$

$$+ \dots + f_{n+1}(t_n) - f_n(t_n); \quad (\text{vide Appendix}), \quad \dots (29.4)$$

where (vide Appendix 1-6)

$$f_1(t) = v_0 A \left[\frac{1}{q} (1 - e^{-qt}) - \frac{1}{p} (1 - e^{-pt}) \right] \quad \dots (30)$$

$$f_2(t_1) = v_0 A^2 \left[\frac{e^{-qt_1}}{q} (1 - A + qt_1) + \frac{e^{-pt_1}}{p} (1 + A + pt_1) \right] \quad \dots (30.1)$$

$$f_3(t_2) = v_0 A^3 \left[\frac{e^{-qt_2}}{q} \left\{ \frac{3}{2} (A - A^2) + \frac{1}{2} (3A - 1) qt_2 - \frac{q^2 t_2^2}{2!} \right\} + \frac{e^{-pt_2}}{p} \left\{ \frac{3}{2} (A + A^2) + \frac{1}{2} (3A + 1) pt_2 + \frac{p^2 t_2^2}{2!} \right\} \right] \quad \dots (30.2)$$

and so on, where A stands for $(q+p)/(p-q)$.

The first term of eq (29.4) is zero for negative values of time; for positive value, i.e., during $0 < t < \theta_1$

$$y_a = f_1(t) \quad \dots (31.1)$$

After time $t = \theta_1$ the second term no longer vanishes, so, during $\theta_1 < t < 2\theta_1$,

$$y_a = f_1(t) + f_2(t_1) - f_1(t_1); \quad \dots (31.2)$$

during $2\theta_1 < t < 3\theta_1$,

$$y_a = f_1(t) + f_2(t_1) - f_1(t_1) + f_3(t_2) - f_2(t_1); \quad \dots (31.3)$$

and so on.

The values of y_a at different intervals, as given by eqs. (31) and (30), are same as obtained previously in a different paper ⁴ following different methods.

From eq (21.2) we have as $\coth \frac{Db}{c} \rightarrow 1$ when b is very large,

$$\begin{aligned} -P &= Eu = \frac{T}{c} \left(\coth \frac{Da}{c} + 1 \right) y_a' \\ &= \frac{2T}{c} (1 + e^{-D\theta_1} + e^{-2D\theta_1} + \dots + e^{-nD\theta_1}) y_a' \\ &= \frac{2T}{c} \left\{ f_1'(t) + f_2'(t_1) + f_3'(t_2) + \dots + f_{n+1}'(t_n) \right\}. \quad \dots (32) \end{aligned}$$

So, neglecting the sign for the time being (as $P = Eu$), we get the expression for pressures at different intervals.

$$\begin{aligned} P_1 &= \frac{2T}{c} f_1'(t), \\ &= 2\rho v_0 c A (e^{-qt} - e^{-pt}); \quad \dots (33.1) \end{aligned}$$

$$\begin{aligned} P_2 &= \frac{2T}{c} \left[f_1'(t) + f_2'(t_1) \right], \\ &= P_1 + 2\rho v_0 c A^2 \left[e^{-qt_1} (A - qt_1) - e^{-pt_1} (A + pt_1) \right]; \quad \dots (33.2) \end{aligned}$$

$$\begin{aligned}
 P_3 &= -\frac{2T}{c} \left[f_1'(t) + f_2'(t_1) + f_3'(t_2) \right], \\
 &= P_2 + 2\rho v_0 c A^3 \left[e^{-qt_2} \left\{ \frac{1}{2}(3A^2 - 1) - \frac{1}{2}(3A + 1)qt_2 + \frac{q^2 t_2^2}{2!} \right\} \right. \\
 &\quad \left. - e^{-pt_2} \left\{ \frac{1}{2}(3A^2 - 1) + \frac{1}{2}(3A - 1)pt_2 + \frac{p^2 t_2^2}{2!} \right\} \right]; \quad \dots \quad (33.3)
 \end{aligned}$$

and so on.

(b) The values of q and p , as have been found, are already given in eq. (29.2). Now, when

$$\left(\frac{EC}{2T} \right)^2 = \frac{4E}{m}, \text{ i.e., } \frac{16\rho}{m} = \frac{E}{T},$$

the same eq. gives

$$q = p = \frac{EC}{4T} = \sqrt{\frac{E}{m}} \quad \dots \quad (34.1)$$

and

$$D_1 = D_2 = D + q. \quad \dots \quad (34.2)$$

So eq. (29.3) becomes, with the help of eq. (34.1),

$$\begin{aligned}
 y_n &= \left[\frac{2q}{(D+q)^2} + \left\{ \frac{4q^2 D}{(D+q)^4} - \frac{2q}{(D+q)^2} \right\} e^{-D\theta_1} + \left\{ \frac{8q^3 D^2}{(D+q)^6} - \frac{4q^2 D}{(D+q)^4} \right\} e^{-2D\theta_1} \right. \\
 &\quad \left. + + + \dots + \left\{ \frac{(2q)^n D^{n-1}}{(D+q)^{2n}} - \frac{(2q)^{n-1} D^{n-2}}{(D+q)^{2(n-1)}} \right\} e^{-(n-1)D\theta_1} \right]. \quad \dots \quad (35.1)
 \end{aligned}$$

$$= f_1(t) + f_2(t_1) - f_1(t_1) + f_3(t_2) - f_2(t_2) + \dots + f_n(t_{n-1}) - f_{n-1}(t_{n-2}), \quad \dots \quad (35.2)$$

where (*vide* Appendix 1-9)

$$f_1(t) = \frac{2v_0}{q} \left[1 - e^{-qt} (1 + qt) \right] \quad \dots \quad (36.1)$$

$$f_2(t_1) = \frac{4v_0}{q} e^{-qt_1} \frac{(qt_1)^3}{3!} \quad \dots \quad (36.2)$$

$$f_3(t_2) = \frac{8v_0}{q} e^{-qt_2} \left\{ \frac{(qt_2)^4}{4!} - \frac{(qt_2)^5}{5!} \right\} \quad \dots \quad (36.3)$$

...

...

...

...

...

...

$$f_n(t_{n-1}) = \frac{2^n v_0}{q} e^{-qt_{n-1}} \left[\frac{(qt_{n-1})^{n+1}}{(n+1)!} - {}^{n-2}C_{n-1} \frac{(qt_{n-1})^{n+2}}{(n+2)!} + - \dots \right. \\ \left. + (-)^{r-1} {}^{n-2}C_{r-1} \frac{(qt_{n-1})^{n+r}}{(n+r)!} + - + - \dots \right. \\ \left. + (-)^{n-2} \frac{(qt_{n-1})^{2n-2}}{(2n-2)!} \right]. \quad \dots \quad (36.4)$$

The values of y_a at different intervals are given by eqs. (31) and (36) and the corresponding expressions for pressures as in eqs. (33) are given below, with the help of eqs. (36),

$$P_1 = \frac{2T}{c} f_1'(t) = 4\rho v_0 c e^{-qt} qt; \quad \dots \quad (37.1)$$

$$P_2 = P_1 + \frac{2T}{c} f_2'(t_2) = P_1 + 8\rho v_0 c e^{-qt_1} \left\{ \frac{(qt_1)^2}{2!} - \frac{(qt_1)^3}{3!} \right\}; \quad \dots \quad (37.2)$$

$$P_3 = P_2 + \frac{2T}{c} f_3'(t_2) = P_2 + 16\rho v_0 c e^{-qt_2} \left\{ \frac{(qt_2)^3}{3!} - 2 \frac{(qt_2)^4}{4!} + \frac{(qt_2)^5}{5!} \right\}; \dots \quad (37.3)$$

$$P_4 = P_3 + \frac{2T}{c} f_4'(t_3) = P_3 + 32\rho v_0 c e^{-qt_3} \left\{ \frac{(qt_3)^4}{4!} - 3 \frac{(qt_3)^5}{5!} \right. \\ \left. + 3 \frac{(qt_3)^6}{6!} - \frac{(qt_3)^7}{7!} \right\}; \quad \dots \quad (37.4)$$

...

$$P_n = P_{n-1} + \frac{2T}{c} f_n'(t_{n-1}) \\ = P_{n-1} + 2^{n+1} \rho v_0 c e^{-qt_{n-1}} \sum_{r=1}^n (-)^{r-1} {}^{n-1}C_{r-1} \frac{(qt_{n-1})^{n+r-1}}{(n+r-1)!}; \quad (37.5)$$

(c) When $\left(\frac{Ec}{2T} \right)^2 < \frac{4E}{m}$, i.e., $\frac{16\rho}{m} < \frac{E}{T}$, both q and p become complex quantities, from eq. (29.2)

$$[q, p] = \mu \mp iv,$$

where $\mu = \frac{E}{4} \frac{c}{T}, v = \frac{1}{2} \sqrt{\frac{4E}{m} - \left(\frac{Ec}{2T} \right)^2}.$... (38)

Now putting these values of q and p in eqs. (30) we have

$$f_1(t) = \frac{2\mu}{v} v_0 \left[\frac{v}{\mu^2 + v^2} - \frac{1}{\sqrt{\mu^2 + v^2}} e^{-\mu t} \sin \left(vt + \tan^{-1} \frac{v}{\mu} \right) \right]; \quad \dots \quad (39'1)$$

$$f_2(t_1) = \frac{2\mu^2}{v^3} v_0 e^{-\mu t_1} \left[\sin vt_1 - vt_1 \cos vt_1 \right]; \quad \dots \quad (39'2)$$

$$f_3(t_2) = \frac{\mu^3}{v^5} v_0 e^{-\mu t_2} \left[\sqrt{(\mu^2 + v^2)} \left\{ v^2 t_2^2 \cdot \sin \left(vt_2 - \tan^{-1} \frac{v}{\mu} \right) + vt_2 \cos \left(vt_2 - \tan^{-1} \frac{v}{\mu} \right) \right\} + \mu \left\{ 2vt_2 \cos vt_2 - 3 \sin vt_2 \right\} \right]; \quad \dots \quad (39'3)$$

and by the help of eqs. (33) and (39) we have

$$P_1 = 4\rho v_0 c \frac{\mu}{v} e^{-\mu t} \sin vt; \quad \dots \quad (40'1)$$

$$P_2 = P_1 + 4\rho v_0 c \frac{\mu^2}{v^3} e^{-\mu t_1} \left[\sqrt{\mu^2 + v^2} \cdot vt_1 \cos \left(vt_1 - \tan^{-1} \frac{v}{\mu} \right) - \mu \sin vt_1 \right]; \quad (40'2)$$

$$P_3 = P_2 + 2\rho v_0 c \frac{\mu^3}{v^5} e^{-\mu t_2} \left[\mu \left\{ (3\mu - 2v^2 t_2) \sin vt_2 - (1 + 2\mu t_2)v \cos vt_2 \right\} + \sqrt{\mu^2 + v^2} \left\{ (v^2 t_2^2 - \mu t_2 + 1) \cdot v \cos \left(vt_2 - \tan^{-1} \frac{v}{\mu} \right) - (\mu t_2^2 + t_2)v^2 \sin \left(vt_2 - \tan^{-1} \frac{v}{\mu} \right) \right\} \right]; \quad \dots \quad (40'3)$$

and so on.

Finite string : Hammer strikes at the mid-point. Now in this case $b=a$ and eq. (21'3) becomes

$$F(D) = D + \left(\frac{2T}{Ec} D^2 + \frac{2T}{mc} \right) \coth \frac{Da}{c} \\ = \frac{D_1 D_2}{(q+p)(1-e^{-D\theta_1})} \left[1 - \left\{ \frac{2(q+p)D}{D_1 D_2} - 1 \right\} e^{-D\theta_1} \right]. \quad \dots \quad (41)$$

Therefore, from eq. (21),

$$y_a = \frac{(q+p)(1-e^{-D\theta_1})}{D_1 D_2} \left[1 - \left\{ \frac{2(q+p)D}{D_1 D_2} - 1 \right\} e^{-D\theta_1} \right]^{-1} \quad \dots \quad (42)$$

where, as before

$$D_1 D_2 \equiv (D+q)(D+p) \equiv D^2 + \frac{Ec}{2T} D + \frac{E}{m},$$

and, $-q$ and $-p$ are the roots of the eq.

$$D_1 D_2 = 0.$$

From eq. (42),

$$\begin{aligned} y_a &= \frac{(q+p)}{D_1 D_2} \left[1 + \left\{ \frac{2(q+p)D}{D_1 D_2} - 2 \right\} e^{-D\theta_1} + \left\{ \left(\frac{2(q+p)D}{D_1 D_2} - 1 \right)^2 \right. \right. \\ &\quad \left. \left. - \left(\frac{2(q+p)D}{D_1 D_2} - 1 \right) \right\} e^{-2D\theta_1} + \dots + \left\{ \left(\frac{2(q+p)D}{D_1 D_2} - 1 \right)^n \right. \right. \\ &\quad \left. \left. - \left(\frac{2(q+p)D}{D_1 D_2} - 1 \right)^{n-1} \right\} e^{-nD\theta_1} \right] v_0; \quad \dots (43.1) \\ &= \left[\frac{(q+p)}{D_1 D_2} + \left\{ \frac{2(q+p)^2 D}{D_1^2 D_2^2} - \frac{2(q+p)}{D_1 D_2} \right\} e^{-D\theta_1} + \left\{ \frac{4(q+p)^3 D^2}{D_1^3 D_2^3} \right. \right. \\ &\quad \left. \left. - \frac{6(q+p)^2 D}{D_1^2 D_2^2} + \frac{2(q+p)}{D_1 D_2} \right\} e^{-2D\theta_1} + \left\{ \frac{8(q+p)^4 D^3}{D_1^4 D_2^4} - \frac{16(q+p)^3 D^2}{D_1^3 D_2^3} \right. \right. \\ &\quad \left. \left. + \frac{10(q+p)^2 D}{D_1^2 D_2^2} - \frac{2(q+p)}{D_1 D_2} \right\} e^{-3D\theta_1} + \dots + \left\{ 2^n \frac{(q+p)^{n+1} D^n}{D_1^{n+1} D_2^{n+1}} \right. \right. \\ &\quad \left. \left. - 2^{n-1} \cdot (n+1) \cdot \frac{(q+p)^n D^{n-1}}{D_1^n D_2^n} + \dots + (-)^r \cdot ({}^n C_r + {}^{n-1} C_{r-1}) \cdot 2^{n-r} \cdot \frac{(q+p)^{n-r+1} D^{n-r}}{D_1^{n-r+1} D_2^{n-r+1}} \right. \right. \\ &\quad \left. \left. + \dots + (-)^n \frac{2(q+p)}{D_1 D_2} \right\} e^{-nD\theta_1} \right] v_0; \quad \dots (43.2) \end{aligned}$$

$$\begin{aligned} &= f_1(t) + 2f_2(t_1) - 2f_1(t_1) + 4f_3(t_2) - 6f_2(t_2) + 2f_1(t_2) + 8f_4(t_3) - 16f_3(t_3) \\ &\quad + 10f_2(t_3) - 2f_1(t_3) + \dots + 2^n f_{n+1}(t_n) - 2^{n-1} \cdot (n+1) f_n(t_n) - \dots \\ &\quad + (-)^r ({}^n C_r + {}^{n-1} C_{r-1}) 2^{n-r} f_{n-r+1}(t_n) - \dots + (-)^n 2f_1(t_n). \quad \dots (43.3) \end{aligned}$$

The values of these functions, when $\left(\frac{Ec}{2T} \right)^2 > \frac{4E}{m}$ are given by eqs. (30)

when $\left(\frac{Ec}{2T} \right)^2 = \frac{4E}{m}$ are given by eqs. (36), and when $\left(\frac{Ec}{2T} \right)^2 < \frac{4E}{m}$ are given by eqs. (39).

As before, the displacement of the struck point during contact in different intervals, can very easily be obtained from eq. (43.3).

$$\begin{array}{ll} \text{During} & 0 < t < \theta_1 \\ & y_a = f_1(t) \end{array} \quad \dots \quad (44'1)$$

$$\begin{array}{ll} \text{During} & \theta_1 < t < 2\theta_1 \\ & y_a = f_1(t) + 2f_2(t_1) - 2f_1(t_1), \end{array} \quad \dots \quad (44'2)$$

$$\begin{array}{ll} \text{During} & 2\theta_1 < t < 3\theta_1 \\ & y_a = f_1(t) + 2f_2(t_1) - 2f_1(t_1) + 4f_3(t_2) - 6f_2(t_2) + 2f_1(t_2), \end{array} \quad \dots \quad (44'3)$$

and so on.

The pressure exerted by the hammer is numerically equal to Eu , which by the help of eq. (21.2), as $b=a$ in this case, is given by

$$\begin{aligned} P &= \frac{2T}{c} \coth \frac{Da}{c} \cdot y_a', \\ &= \frac{2T}{c} \left[1 + 2e^{-D\theta_1} + 2e^{-2D\theta_1} + 2e^{-3D\theta_1} + \dots \right] y_a'. \end{aligned} \quad \dots \quad (45)$$

The eq. (45), by the help of (43.3),

$$\begin{aligned} P &= f_1'(t) + 2f_2'(t_1) + 4f_3'(t_2) - 2f_2'(t_2) + 8f_4'(t_3) \\ &\quad - 8f_3'(t_3) + 2f_2'(t_3) + \dots \end{aligned} \quad \dots \quad (46)$$

Whence we get

$$P_1 = \frac{2T}{c} f_1'(t); \quad \dots \quad (47.1)$$

$$P_2 = P_1 + \frac{4T}{c} f_2'(t_1); \quad \dots \quad (47.2)$$

$$P_3 = P_2 + \frac{4T}{c} \left[2f_3'(t_2) - f_2'(t_2) \right]; \quad \dots \quad (47.3)$$

$$P_4 = P_3 + \frac{4T}{c} \left[4f_4'(t_3) - 4f_3'(t_3) + f_2'(t_3) \right]; \quad \dots \quad (47.4)$$

and so on.

In order to study the pressure functions obtained in this paper, we consider a particular case of a string and hammer system. The hammer, of mass 21.2 gms, strikes at a distance $l/10$ from one of the fixed ends of steel string, of length 600 cms., of linear density .05 gm./cm., stretched under a tension of 38.5 kilo-gm. weight.

The curves in figure 1 show the variation of P with ct . The dotted curve marked (a) is for the hard hammer. This is obtained with the help of the exact formula obtained in Part I or by the help of formula (33) for $E=\infty$. The curve (a) shows that the impact ceases in the fourth epoch. And the duration of impact obtained graphically is 1.51×10^{-2} sec., the corresponding observed value being 1.48×10^{-2} seconds, however, is very good agreement.

Next we consider the case of the elastic hammer for two different values of the elastic constant. The curve (b) represents P - ct curve for $\frac{E}{T} = 1$. Here the formula (33) is used, as this values of $\frac{E}{T}$ makes q and p given by eq. (29.2) real and unequal. The pressure is found to terminate during the fourth epoch, but the duration of impact is greater than what is given for the hard hammer. The curve (c) represents the same for $\frac{E}{T} = 3.77 \times 10^{-2}$. Here the formula (37) is used,

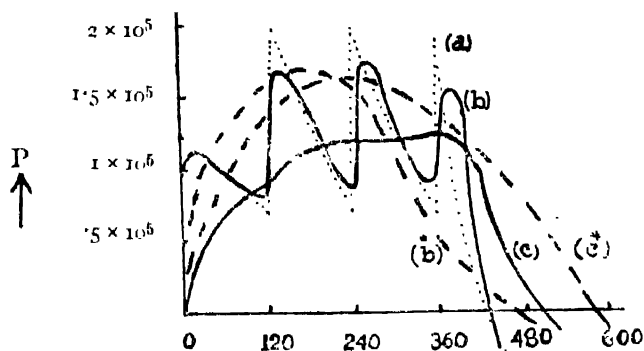


FIGURE 1

as this value of $\frac{E}{T}$ makes q and p real and equal. The pressure terminates during the fifth epoch. Any value of $\frac{E}{T}$ less than .0377 for, the present system, will make q and p imaginary and unequal, and so eq. (40) is to be used. Now comparing the curves (a), (b), (c), we find that, as the hard hammer is replaced by an elastic one, the discontinuous periodic rises of pressure lose their sharp angularities and well-rounded humps appear instead. As the value of E is diminished, humps become less and less pronounced. Further, we find that the duration of impact gradually increases as the hardness of the striking hammer gradually decreases. But the duration is not much affected with the slight diminution of the hardness, and the appreciable change of hardness to a smaller value will cause a sensible increase of the duration of impact.

The relative intensities of over-tones will increase with the rise of the values of pressure-maxima of these curves. So the over-tones grow feebler as the

hardness of the hammer decreases, and the corresponding delayed separation of the hammer from the string will further damp the growth of the over-tones. Again, we find that the pressure exerted by the hammer and the corresponding rises of the maxima are directly proportional to the *impinging velocity*. Hence, for a given elastic constant of the hammer, the over-tones grow feebler as the impinging velocity changes from a larger to smaller value. In other words, for a large value of the impinging velocity, the hammer undergoes more compression than what is expected from Hooke's law. So its effective hardness increases, and tone produced loses its softness. This fact is evident from the photograph of the vibration of the string as obtained by the writer ⁵ (Fig. d, Pt. 27).

The curves (b) and (c), in broken lines, represent the case (b) and (c) respectively drawn by the help of the approximate formula (27). Though this formula is more general than what is obtained by Bhargaba-Ghosh ² and Das, ³ yet its validity is questionable. These approximate curves give greater values of the duration of contact than those obtained by the exact formula. As the area bounded by the curve and the time axis is proportional to the total change of momentum, the area bounded by the exact and approximate curves should be nearly equal. But comparing (b), (b) and (c), (c) it is found that the discrepancy becomes more and more violent as the elastic constant gradually decreases. The derivation of the formula is based upon the solution of the eq. $F(D)=0$ given in eqn. (21.3). This is reduced to a cubic equation on the assumption that a is small and E is large (*vide* eq. 24).

For small values of E , $F(D)$ cannot be replaced by a cubic, but the equation of higher degree will come in. So the approximate formula (37) fails for small values of E and for large values of a .

My best thanks are due to Professor K. C. Kar, D.Sc., for the interest he took in the work.

APPENDIX

$$\begin{aligned}
 (1) \quad & \frac{(q+p)^n D^{n-1}}{(D+q)^n (D+p)^n} \cdot v_0 = f_n(t) \\
 & = (q+p)^n D^{n-2} \cdot \frac{D}{D_1^n D_2^n} \cdot v_0 \\
 & = (q+p)^n \cdot D^{n-2} \cdot \beta^n \left[\sum_{r=1}^n (-)^{r-1} \frac{\Gamma(n+r-1)}{\Gamma(n)\Gamma(r)} \cdot \beta^{r-1} \cdot \frac{D}{D_1^{n-r-1}} \right. \\
 & \quad \left. + (-)^n \sum_{r=1}^n \frac{\Gamma(n+r-1)}{\Gamma(n)\Gamma(r)} \cdot \beta^{r-1} \cdot \frac{D}{D_2^{n-r+1}} \right] \cdot v_0
 \end{aligned}$$

$$\begin{aligned}
 &= A^n v_0 D^{n-2} \left[\sum_{r=1}^n (-)^{r-1} \frac{\Gamma(n+r-1)}{\Gamma(n)\Gamma(r)} \cdot \beta^{r-1} e^{-qt} \cdot \frac{t^{n-r}}{(n-r)!} \right. \\
 &\quad \left. + (-)^n \sum_{r=1}^n \frac{\Gamma(n+r-1)}{\Gamma(n)\Gamma(r)} \cdot \beta^{r-1} e^{-pt} \cdot \frac{t^{n-r}}{(n-r)!} \right] \\
 &= A^n v_0 \left[\sum_{r=1}^n (-)^{r-1} \frac{\Gamma(n+r-1)}{\Gamma(n)\Gamma(r)} \beta^{r-1} e^{-qt} \cdot (D-q)^{n-2} \cdot \frac{t^{n-r}}{(n-r)!} \right. \\
 &\quad \left. + (-)^n \sum_{r=1}^n \frac{\Gamma(n+r-1)}{\Gamma(n)\Gamma(r)} \beta^{r-1} e^{-pt} \cdot (D-p)^{n-2} \cdot \frac{t^{n-r}}{(n-r)!} \right]
 \end{aligned}$$

and

$$\begin{aligned}
 (1.1) \quad f_n'(t) &= D \cdot f_n(t) \\
 &= A^n v_0 \left[\sum_{r=1}^n (-)^{r-1} \frac{\Gamma(n+r-1)}{\Gamma(n)\Gamma(r)} \beta^{r-1} e^{-qt} (D-q)^{n-1} \cdot \frac{t^{n-r}}{(n-r)!} \right. \\
 &\quad \left. + (-)^n \sum_{r=1}^n \frac{\Gamma(n+r-1)}{\Gamma(n)\Gamma(r)} \beta^{r-1} e^{-pt} (D-p)^{n-1} \cdot \frac{t^{n-r}}{(n-r)!} \right]
 \end{aligned}$$

also

$$(1.2) \quad f_n(t) e^{-Dn\theta_1} = f_n(t - n\theta_1)$$

$$\text{where} \quad D_1 = (D+q), \quad D_2 = (D+p), \quad \beta = \frac{1}{p-q} \quad \text{and} \quad A = \beta(g+p),$$

$$\text{So, } \beta q = \frac{1}{2}(A-1), \text{ and } \beta p = \frac{1}{2}(A+1).$$

$$\begin{aligned}
 (2) \quad \frac{(q+p)}{D_1 D_2} v_0 &= f_1(t) \\
 &= A v_0 \left[\frac{1}{D_1} - \frac{1}{D_2} \right] = A v_0 \left[\frac{1}{q} (1 - e^{-qt}) - \frac{1}{p} (1 - e^{-pt}) \right]
 \end{aligned}$$

$$\begin{aligned}
 (3) \quad \frac{(q+p)^2 D}{D_1^2 D_2^2} v_0 &= f_2(t), \quad \text{putting } n=2 \text{ in (1),} \\
 &= A^2 v_0 \left[\frac{e^{-qt}}{q} (1 - A + qt) + \frac{e^{-pt}}{p} (1 + A + pt) \right]
 \end{aligned}$$

$$\begin{aligned}
 (4) \quad \frac{(q+p)^3 D^2}{D_1^3 D_2^3} v_0 &= f_3(t), \quad \text{for } n=3 \text{ in (1),} \\
 &= A^3 v_0 \left[\frac{e^{-qt}}{q} \left\{ \frac{3}{2} A(1+A) + \frac{1}{2} (3A-1)qt - \frac{q^2 t^2}{2!} \right\} \right. \\
 &\quad \left. + \frac{e^{-pt}}{p} \left\{ \frac{3}{2} A(1+A) + \frac{1}{2} (3A+1)pt + \frac{p^2 t^2}{2!} \right\} \right]
 \end{aligned}$$

$$\begin{aligned}
 (5) \quad & \frac{(q+p)^4 D^3}{D_1^3 D_2^3} v_0 = f_4(t), \quad \text{for } n=4 \text{ in (1),} \\
 & = A v_0 \left[\frac{e^{-qt}}{q} \left\{ \frac{1}{2}(1-A)(5A^2-1) + (5A^2-6A+2)qt - (2A-1) \frac{q^2 t^2}{2!} + \frac{q^3 t^3}{3!} \right\} \right. \\
 & \quad \left. + \frac{e^{-pt}}{p} \left\{ \frac{1}{2}(1+A)(5A^2+1) + (5A^2+6A+2)pt + (2A+1) \frac{p^2 t^2}{2!} + \frac{p^3 t^3}{3!} \right\} \right]
 \end{aligned}$$

$$\begin{aligned}
 (6) \quad & \frac{(q+p)^5 D^4}{D_1^3 D_2^3} v_0 = f_5(t), \quad \text{for } n=5 \text{ in (1),} \\
 & = A^5 v_0 \left[\frac{e^{-qt}}{q} \left\{ \frac{5}{8}(A-1)(7A^2-3) + \frac{1}{8}(35A^3-15A^2-71A+59)qt \right. \right. \\
 & \quad \left. \left. - \frac{3}{4}(5A^2-1) \frac{q^2 t^2}{2!} + \frac{1}{2}(5A-1) \frac{q^3 t^3}{3!} - \frac{q^4 t^4}{4!} \right\} \right. \\
 & \quad \left. + \frac{e^{-pt}}{p} \left\{ \frac{5}{8}(A+1)(7A^2-3) + \frac{1}{8}(35A^3+15A^2-71A-59)pt \right. \right. \\
 & \quad \left. \left. + \frac{3}{4}(5A^2-1) \frac{p^2 t^2}{2!} + \frac{1}{2}(5A-1) \frac{p^3 t^3}{3!} + \frac{p^4 t^4}{4!} \right\} \right]
 \end{aligned}$$

and so on.

$$(7) \quad \text{When } q=p, \quad (1) \text{ becomes}$$

$$\begin{aligned}
 & \frac{(2q)^n D^{n-1}}{(D+q)^{2n}} \cdot v_0 = f_n(t) \\
 & = (2q)^n D^{n-2} \frac{D}{(D+q)^{2n}} v_0 = (2q)^n v_0 D^{n-1} e^{-qt} \frac{t^{2n-1}}{(2n-1)!} \\
 & = (2q)^n v_0 e^{-qt} (D-q)^{n-2} \frac{t^{2n-1}}{(2n-1)!} - 2^n v_0 \frac{e^{-qt}}{q} \left[\frac{(qt)^{n+1}}{(n+1)!} - {}^{n-2}C_1 \frac{(qt)^{n+2}}{(n+2)!} \right. \\
 & \quad \left. + - + - \dots + (-)^{n-2} \frac{(qt)^{2n-2}}{(2n-2)!} \right]
 \end{aligned}$$

$$(8) \quad \frac{2q}{(D+q)^2} v_0 = f_1(t), \quad \text{for } q=p \text{ in (2)}$$

$$\begin{aligned}
 & = \frac{2}{q} \left[\frac{q}{D+q} - q \cdot \frac{D}{(D+q)^2} \right] \cdot v_0 \\
 & = \frac{2}{q} \left[1 - \frac{D}{(D+q)} - q \frac{D}{(D+q)^2} \right] \cdot v_0 \\
 & = \frac{2v_0}{q} \left[1 - e^{-qt} (1+qt) \right]
 \end{aligned}$$

$$(9) \quad -\frac{(2q)^2 D}{(D+q)^4} = f_2(t) \quad \text{for } n=2 \quad \text{in (7)}$$

$$= 4v_0 \frac{c^{-qt}}{q} \cdot \frac{(qt)^3}{3!}$$

(10) $f_3(t)$, $f_4(t)$, $f_5(t)$ etc., are obtained by putting $n=3, 4, 5$, etc., respectively.

DEPARTMENT OF PHYSICS,
BURDWAN RAJ COLLEGE,
BURDWAN.

REFERENCES

- ¹ Ghosh, M., *Ind. Jour Phys.*, **12**, 317 (1938).
- ² Bhargava, S. and Ghosh, R. N., *Phil. Mag.*, **47**, 1141 (1924).
- ³ Das, P., *Proc. Phys. Soc.*, **40**, 29 (1927).
- ⁴ Ghosh, M., *Ind. Jour. Phys. Math.*, **3**, 15 (1932) ; *Phil. Mag.*, **17**, 521 (1934).
- ⁵ Ghosh, M., *Ind. J. Phys.*, **7**, 365 (1932).

THE LOWER IONOSPHERE*

BY S. K. MITRA, J. N. BHAR

AND

S. P. GHOSH

(Received for publication, Dec. 9, 1938.)

ABSTRACT. It is now recognised that layers of ionization maxima capable of reflecting radio waves, not unlike those existing in the upper ionosphere, are also formed in the middle and the lower atmosphere. The mode of reflection of radio waves in these dense regions of the atmosphere must be different from that in the upper E and F ionospheric regions where the collisional frequency is small compared with the exploring wave frequency and the refractive index has a value less than unity. In order to investigate the mode of reflection from these lower ionized regions, curves have been drawn depicting the variations of μ (refractive index) and κ (absorption coefficient) with N (electron density) for various values of ν (collisional frequency) appropriate for the dense middle atmospheric regions. It is found that near certain values of N depending on the value of the collisional frequency, μ increases rapidly with increasing N . If for an ionized layer in the middle or the lower atmosphere N has a value corresponding to any of these, then near its lower boundary N will increase with height and may produce large variation of μ within distances small compared with the exploring wave-length (measured in vacuum). Such regions of rapidly varying μ will be able to cause reflection of radio waves. Probable reflection coefficients of such regions are calculated with the help of the dispersion and the absorption curves using the expression of reflection coefficient for metallic surfaces. Cases considered are $\nu = 10^8$, 10^9 and 10^{10} per second for wave frequency 4 Mc./sec. Calculations show that for the above values of ν , the corresponding values of N near which μ rapidly changes are $10^{8.5}$, $10^{7.5}$ and $10^{6.5}$ per c.c.

Possible modes of formation of the ionized regions are also considered by applying Pannekoek's method to the cases of the first ionization potentials of O_2 (12.2 e.v.) and N_2 (15.5 e.v.). It is found that the height of the ionization maximum for N_2 agrees with the height of the E_2 layer (140 km.). Similar calculation for O_2 yields an ionization maximum the height of which corresponds to the D layer (55 km.). Lack of knowledge of the ionization potentials of O_3 prevents calculation for the ionization maximum which may possibly be produced at lower heights corresponding to the C_2 layer (30 km.).

1. INTRODUCTION.

Recent investigations show that besides the two main strata of the ionosphere—the E and the F layers in the upper atmosphere—ionized layers are also

* Communicated by the Indian Physical Society. Some portions of this paper were originally drafted by the senior author in collaboration with Dr. H. Rakshit. The paper as presented now is, however, on a plan different from that originally contemplated. Dr. Rakshit being abroad, is unable to collaborate with us in the present communication.

formed in the middle and the lower atmosphere which may, under suitable conditions, reflect radio waves. Evidence on this point was obtained in 1936 from three independent observations made in three different countries of the world. It is now convenient to divide the ionosphere into two parts and to designate the ionized regions above 90 km. collectively as the upper ionosphere and those below as the lower ionosphere. In the following communication an attempt will be made to review the present position of our knowledge regarding the lower ionosphere and also to discuss some of its properties.

The existence of some ionized region below E —the lowermost layer of the upper ionosphere—though not definitely proved by direct experimental observation, was for a long time suspected. Various effects connected with the variation of signal strength and of the strength of the atmospherics from daylight to night hours pointed to the formation of an absorbing ionized region below the E layer.^{1,2} The most casual radio listener notices an increase of atmospherics with the fall of darkness and, simultaneously with it, enhancement of the signal strength of medium wave stations at long distances. The natural explanation of this phenomenon is that during hours of sunlight the comparatively dense atmosphere below the E layer is ionized where, on account of frequent collisions between electrons and ions and the neutral gas molecules, radio waves are strongly absorbed. When the ionizing solar radiation is withdrawn with the fall of darkness the ionization disappears quickly on account of rapid recombination and absorption of radio waves ceases. Though the existence of such an absorbing ionized region was recognised by radio investigators there was some difference of opinion as to its actual location. Appleton in 1928 suggested that the layer was situated at about 60 km. height and that it could also deviate radio waves.¹ He designated it as D layer. This view was not, however, pressed in subsequent years by Appleton's school of investigators particularly because direct proof regarding its existence, such as that furnished by radio "echoes," was lacking. The tendency till lately had therefore been to regard the absorbing ionized region not as a distinct and separate region of maximum ionization but as a sort of "tail" or continuation of the E region formed during daytime.³

Mitra and Syam, however, in 1935 announced that they had detected regular reflection of radio waves at vertical incidence from an equivalent height of about 55 km.⁴ About a year later on March 8, 1936, Mitra and Bhar made a further announcement that they had recorded echoes of radio waves from still lower heights.⁵ (Actual photographs of echoes received from these low heights were published shortly afterwards by Rakshit and Bhar⁶). Soon after Colwell and Friend⁷ from West Virginia, U.S.A., reported the recording of echoes from regions between 55 and 5 km. and a little later Watson Watt, Bainbridge-Bell, Wilkins and Bowen⁸ announced that they also had occasionally recorded echoes from similar heights.

These observations from three independent sources situated in three widely different parts of the world showed that the atmosphere below 90 km. is also stratified particularly during daytime into ionized layers like the upper ionosphere. The layers were found to be grouped roughly in three different heights; one at about 55 km. another round 30 km. and the third in the upper troposphere between 5 and 15 km. It is now generally agreed that the 55 km. layer, which might be said to have been rediscovered by Mitra and Syam, should retain the original designation—the D layer—as suggested by Appleton¹ and that the 30 km. and the lower layers should be called C regions—C₂ and C₁ for instance.

Reflections of radio waves from these low heights raise points of great theoretical interest. Firstly, what is the mechanism of the reflections? The usual Eccles-Larmor theory of bending of radio waves by an ionized atmosphere is, on account of the high collisional frequency between the electrons and ions and the gas particles, certainly inoperative. Secondly, in any mode of reflection in which a large density of ions or electrons is necessary (as it will presently be shown to be in the present case) the question arises—What is the origin of the ionization at such low heights of comparatively high atmospheric density?

2. MODE OF REFLECTION FROM LOWER IONOSPHERIC LAYERS.

The conditions of the usual Eccles-Larmor mode of reflection is that the refractive index μ should be less than unity—the actual minimum value of μ necessary (for total reflection) depending upon the angle of incidence of the waves. If the incidence is normal, as is usually the case with ionospheric exploration by the pulse method, μ must be very nearly zero in order that total reflection may occur. Now in a region of high collisional frequency ν such as in the lower ionosphere, $\nu \gg p$, p being the angular wave frequency, and the value of μ can never approach zero. In fact it will be seen from the curves given below that its value may considerably exceed unity. Total reflection for vertical propagation or even for propagation in directions approaching the vertical—for which the necessary condition of reflection is $\mu < 1$ —will thus never take place.

There is, however, another possible mode of reflection in which μ need not approach zero value. The condition for this mode of reflection may be described as *rapid change of μ with increasing electron density within a distance small compared with one vacuum wave-length of the propagated wave*. We will show that in the lower ionosphere where on account of large value of ν , μ is always greater than unity, reflection takes place according to this condition.

In the regions considered by us the collisional frequency ν is much greater than p_H —the gyro-magnetic frequency. The earth's magnetic field will therefore have little effect on the mode of propagation. We can thus find out the values of μ and χ from the simple Eccles-Larmor formula :

$$\left(\mu - i\chi \right)^2 = 1 + \frac{1}{\alpha + i\beta} \quad \dots (1)$$

Separating the real and the imaginary parts we have

$$\mu^2 - \chi^2 = 1 + \frac{\alpha}{\alpha^2 + \beta^2} \quad \dots (2)$$

and

$$2\mu\chi = \frac{\beta}{\alpha^2 + \beta^2} \quad \dots (3)$$

Eliminating χ between (2) and (3) we get

$$2\mu^2 = \sqrt{1 + \frac{2\alpha + 1}{\alpha^2 + \beta^2}} + \frac{\alpha}{\alpha^2 + \beta^2} + 1 \quad \dots (4)$$

$$2\chi^2 = \sqrt{1 + \frac{2\alpha + 1}{\alpha^2 + \beta^2}} - \frac{\alpha}{\alpha^2 + \beta^2} - 1 \quad \dots (5)$$

where

$$\alpha = -\frac{m p^2}{4 \pi N e^2}$$

$$\beta = \frac{m p v}{4 \pi N e^2}$$

μ —refractive index

χ —absorption per length of path $\lambda/2\pi$

e, m —electronic charge and mass

and

p —angular frequency of the exploring waves.

It will be seen that the expression for μ^2 (eqn. 4) can never approach zero for any value of N so long as $v \gg p$. This is also evident from the curves (continuous curves) in figure 1 which depict the relation between μ^2 and N for different values of v as given by eqn. (4). These curves are drawn for a wave frequency of 4 Mc./sec. It will be seen from these curves that near certain values of N , μ^2 increases rapidly with N . Such regions of rapidly increasing μ may cause reflection of radio waves provided that the gradient of ionization is so sharp that large change of μ occurs within a length of path small compared to one vacuum wave-length. This type of reflection may be termed metallic reflection. We can now make an estimate of the reflecting power of the ionized region in these circumstances with the help of the formula⁹

$$\rho^2 = \frac{\mu^2 + \chi^2 + 1 - 2\mu}{\mu^2 + \chi^2 + 1 + 2\mu} \quad \dots (6)$$

where χ is the absorption per length of path $\lambda/2\pi$, λ being one vacuum wave-length.

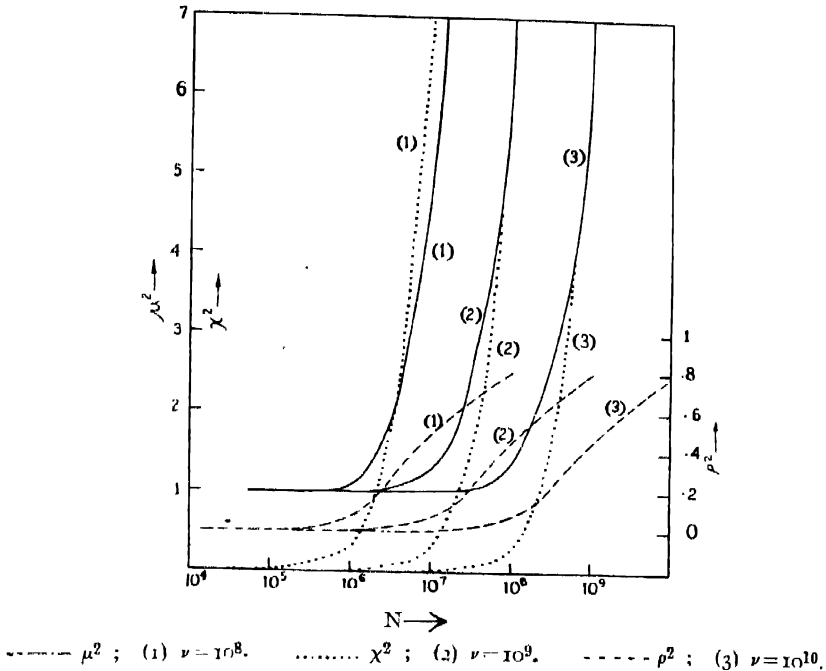


FIGURE 1.

In order to evaluate ρ^2 from this equation a knowledge of χ^2 is required. This is obtained from the curves (dotted) in figure 1 delineating the relation between χ^2 and N drawn with the help of equation (5). The values of ρ^2 for different values of N and for each value of ν are then calculated according to equation (6) and curves drawn therefrom (dashed curves, Fig. 1).

It will be seen in the figure that for each value of ν the $\rho^2 - N$ curve shows abrupt increase in the value of ρ^2 near values of N for which μ^2 also undergoes rapid increase. It is therefore quite possible for reflection of radio waves to occur from such a region even though the collisional frequency be high. An important point should, however, be stressed here. For reflection to occur with appreciable intensity two conditions must hold. Firstly, the change of μ^2 must be considerable within a length of path smaller than one vacuum wave-length and secondly the absorption must be small. Both of these conditions cannot be simultaneously satisfied unless the gradient of ionization is very sharp. If the boundary is diffuse, the ionized region will cause absorption rather than reflection. We suppose that this is the reason why reflections from the lower ionized layers are observed only occasionally.

The curves given in figure 1 enable us to estimate the probable values of the ionic density necessary for appreciable reflection from the ionized regions D, C₂ and C₁ in the lower ionosphere. If we assume an isothermal atmosphere at a temperature of 200° K above the troposphere, the values of ν are 1.91×10^8 , 4.91×10^9 and 5.98×10^{10} per second at levels of 55, 30 and 10 kms, respectively.

Case 1. $\nu=10^8$ — The μ^2 -N curve indicates that rapid increase of μ^2 occurs when N is of the order of $10^{6.5}$. The reflecting power for this value of N is 0.23. In other words, the reflection coefficient ρ , i.e., the ratio of the reflected and incident amplitudes is 0.48, which is quite considerable.

Cases 2 and 3. $\nu=10^9$ and 10^{10} — In these cases, rapid change of μ^2 occurs for values of N of the order of $10^{7.5}$ and $10^{8.5}$ respectively. The reflection coefficient, as defined above, for both these values, is as high as 0.45 nearly.

It is thus seen that reflections from the low heights may occur with sufficient intensity even when the collisional frequency is as high as 10^8 to 10^{10} per second.

3. FORMATION OF IONIZED LAYERS AT LOW HEIGHTS

We will now discuss the possible mode of formation of ionized layers at low heights by the application of Pannekoek's theory.^{10, 11} Apart from the fact that reflections of radio waves are occasionally observed from the lower ionized regions evidence has recently been obtained from a novel phenomenon which definitely shows that solar ultra-violet radiation is capable of producing ionization at levels below the E level. This is the phenomenon of radio fade out in which bright chromospheric eruptions in the sun are found to be accompanied by radio effects such as cessation of ionospheric echoes and strengthening of atmospherics and long wave signals.^{12, 13} These effects can only be explained by the hypothesis that the ultra-violet radiation from the solar eruptions penetrates the denser regions of the atmosphere below the E layer and produces ionization there. It is thus very reasonable to assume that the ionized region in the lower atmosphere above the ozone layer is also produced by penetrating solar ultra-violet radiation.

Our knowledge of the mode of formation of ionized regions in the upper ionosphere will help us to put forward tentative hypothesis regarding the ionizing processes in the lower ionosphere. It is now recognised the each ionization maximum in the upper ionosphere is associated with a particular gaseous constituent of the atmosphere and a particular ionization potential. Thus it has been shown that¹⁴ the F₂ region owes its origin to the photo-ionization of atomic oxygen (13.55 e.v.), the F₁ region to that of N₂ at its second ionization potential (18.67 e.v.), and the E₁ region to that of O₂ also at its second ionization potential (16.5 e.v.). If we take into account the atmospheric constituents below the E layer and also their possible modes of ionization several possibilities present themselves. Firstly, with regard to the ionization potential we have taken into account only the second ionization potentials of N₂ and O₂ when considering the upper atmospheric ionization. The absorptions of wave-lengths corresponding to the first ionization

potentials of these two gases can also be expected to produce corresponding ionization maxima.¹⁴ Again the atmospheric constituents already considered are only N_2 , O_2 and O . Besides these gases we now know that ozone exists in the middle atmosphere between 20 and 50 kms. and possibly atomic nitrogen in the higher levels of the upper atmosphere. The following are therefore the possibilities of the production of layers of ionization maxima besides those discussed above :—

Absorptions of ultraviolet radiations leading to (i) ionization of O_2 by wave-lengths corresponding to its first ionization potential (λ 1012 Å), (ii) ionization by wave-lengths corresponding to the first ionization potential of N_2 (λ 795 Å), (iii) ionization of atomic nitrogen and (iv) ionization of O_3 in the ozonosphere.

Now in order that quantitative calculation of the height of maximum ionization and the ionic density distribution of the various layers corresponding to the above processes be made it is necessary that we know the following for each of the constituents :—

(i) Value of the absorption coefficient of the region of the spectrum of solar radiation corresponding to the appropriate ionization potential and its variation with frequency.

(ii) Distribution of density with height.

The first of the above data is known only approximately for N_2 from experimental observations.¹⁵ For the other gases we can only make rough estimates. This dearth of knowledge makes it difficult to carry out quantitative calculation with any degree of precision. With regard to atomic nitrogen we need not consider its ionization because if atomic nitrogen exists at all it will exist only in the higher regions of the atmosphere. Regarding O_3 our knowledge of its photo-ionization is almost nil, both theoretically and experimentally. We will therefore discuss the possible formation of ionized strata due to the first ionization potentials of N_2 and O_2 only.

For N_2 we will utilise the experimental results of absorption study by Worley and Jenkins.¹⁵ These authors have observed an ionization continuum with the associated Rydberg series of absorption bands corresponding to the first ionization potential (15.5 e.v.) with a column of 0.017 cms. of gas at N.T.P. Now we know from experiments of Hopfield¹⁶ that the absorption by N_2 in the region of wave-lengths corresponding to its second ionization potential is almost complete for path length of a few hundredths of a mm. at N.T.P. It follows therefore that the value of the absorption coefficient in the first case is smaller than that in the second case by a factor of about 3 to 5. In the paper¹¹ by Bhar above referred to the absorption coefficient for wave-length corresponding to the second ionization potential has been taken as 1.0×10^{-18} cm.² per molecule. We may therefore take the absorption coefficient of N_2 for wave lengths corresponding to the first ionization potential as 5×10^{-19} cm.² per molecule.

For O_2 it has not yet been possible to observe, presumably owing to extreme weakness, the absorption continuum for wave-lengths corresponding to the first ionization potential. It is therefore quite reasonable to assume that the absorption is very weak and that the value of the absorption coefficient correspondingly small. As a rough approximation we may take it as 10^{-21} cm.² per molecule which is 10^{-3} times its value at the second ionization potential. This means that appreciable absorption of radiation of the wave-lengths corresponding to the first ionization potential can take place only when the radiation has traversed a path length of about a metre at N.T.P.

Regarding the density distribution of N_2 we will assume that above 100 km. it is in diffusive equilibrium, that is to say, N_2 molecules are distributed independently of other constituents according to Dalton's law. It is now generally assumed that the temperature above 100 km. increases with height. We will, however, take the temperature to be constant having a mean value of $450^\circ K$. Considering the various approximations made regarding the value of the absorption coefficient it may be expected that this further approximation will not lead to large percentage of error. The density of N_2 at 100 km. level will be taken as 2.5×10^{13} molecules per c.c.¹⁷

With regard to O_2 we will have to consider its density distribution with height in the middle atmosphere (15-80 km.) since the ionizing radiation corresponding to its ionization potential (12.2 e.v.) will, on account of its feeble absorption, penetrate into the dense lower regions. Now the density distribution of O_2 is complicated in the first place by the irregular temperature variation in the middle atmosphere—there being a region of high temperature round 45 km. due to ozone absorption and secondly by the rapid decrease of the number of O_2 molecules in the region above 80 km. due to their dissociation. With respect to the latter it has been shown that at a height of about 130 km. molecular oxygen is almost completely replaced by atomic oxygen.¹⁸ It is not however difficult to calculate the density distribution either in the middle atmosphere or in the upper atmosphere between 80 and 130 km., if plausible assumptions regarding the nature of temperature variation and the rate of diminution of O_2 (due to dissociation in the region 80-130 km.) are made. We will assume that the temperature at 35 km. is $208^\circ K$ and that it increases linearly attaining the value of $450^\circ K$ at 55 km. From 55 km. it decreases (again linearly) dropping to the value of $180^\circ K$ at 80 km. From this height the temperature increases upwards. The distribution of density between any two levels within which the temperature is varying linearly may be represented approximately by an expression of the form $e^{-\theta z}$ where θ is a constant depending upon the densities at the two levels. The distribution given by this expression is evidently that of an isothermal region of which the temperature

$T = \frac{k\theta}{mg}$, where k , m and g have the usual meanings. This value of T differs

from the mean value of T in the region between the two levels under consideration and may be called the value of T "appropriate" for that region. We are however led to make this simplifying assumption— T constant—for a particular short interval of region because it is not possible to apply Pannekoek's method when the temperature of the region under consideration is changing with height. The temperature distribution, the calculated values of θ and the calculated "appropriate" values of T for the regions in the middle atmosphere are shown in the accompanying Table.

ASSUMED DISTRIBUTION OF O_2 IN THE REGION
BETWEEN 35 AND 80 km.

Region.	Mean T .	Calculated Value of θ .	"Appropriate" Value of T .
35 to 55 km.	288°K	1.50×10^{-6}	248°K
55 to 80 km	318°K	0.99×10^{-6}	382°K

The densities at the datum levels, namely at 35, 55 and 80 km., used for the calculations are taken from calculations of Ghosh¹⁹ made on the assumption of

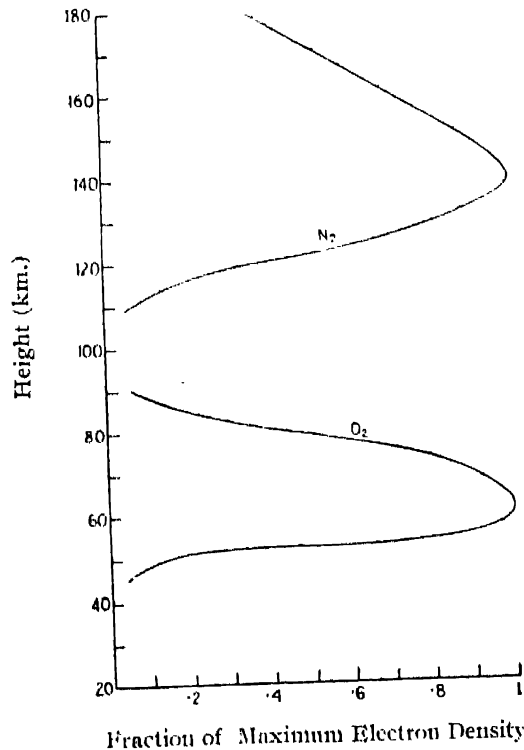


FIGURE 2.

temperature distribution suggested by Martyn and Pulley.²⁰ The density distribution of O_2 between 80 and 130 km. is assumed to be the same as that given in Bhar's paper above referred to.¹¹ The value of θ in this region is taken to be 4.6×10^{-6} . The mean temperature is assumed to be $300^\circ K$.

The results of the calculations carried out with these data are depicted by means of graphs in figure 2 in which the abscissae represent the fractions of the maximum electron density corresponding to a particular constituent.

It will be seen that the ionized layer due to N_2 has its maximum at a height of about 140 km. It is of interest to note that this is approximately the level of maximum ionization of the E_2 layer. We are therefore tempted to suggest that the E_2 layer is due to the photo-ionization of N_2 at its first ionization potential (15.5 e.v.).

The ionization maximum due to O_2 occurs at about 55 km., i.e., much below the E_1 layer. It is quite probable, therefore, that the D layer is formed by the photo-ionization of O_2 at its first ionization potential.

Thus calculations carried out for the first ionization potentials of N_2 and O_2 give us two ionization maxima which may be identified with E_2 and D regions respectively. It is very likely that this latter ionization is enhanced during chromospheric eruptions and produces the radio fade-out effect. If this be so then one has to admit that the so-called D region which causes absorption of radio waves is not a "tail" or a continuation of the E region formed during daytime (as is sometimes supposed) but is a region of ionization maximum distinct from the E-region. As mentioned before the E_1 region is due to the second ionization potential of O_2 while the D region is due to its first ionization potential.

Lack of spectroscopic knowledge of O_3 prevented us from making any calculation regarding the possibility of production of ionization maxima due to this gas. It is quite possible that the C_2 layer at about 30 km., is due to O_3 -ionization.

WIRELESS LABORATORY,
UNIVERSITY COLLEGE OF SCIENCE,
92, UPPER CIRCULAR ROAD,
CALCUTTA.

REFERENCES.

¹ E. V. Appleton, *International Union Scientific Radio Telegraphy*, Part 1, Vol. 1 (1928).

- ² F. V. Appleton and J. A. Ratcliffe, *Proc. Roy. Soc. A*, **128**, 133 (1930); M. A. Bontch Brucwitch, *Nature*, **133**, 175 (1934).
- ³ F. T. Farmer and J. A. Ratcliffe, *Proc. Roy. Soc. A*, **151**, 370 (1935).
- ⁴ S. K. Mitra and P. Syam, *Nature*, **138**, 953 (1935); P. Syam, *Ind. Jour. Phys.*, **10**, 13 (1936).
- ⁵ S. K. Mitra and J. N. Bhar, *Science and Culture*, **1**, 782 (1936).
- ⁶ H. Rakshit and J. N. Bhar, *Nature*, **138**, 283 (1936).
- ⁷ R. C. Collowell and A. W. Friend, *Nature*, **137**, 782 (1936).
- ⁸ R. A. Watson-Watt and others, *Nature*, **137**, 866 (1936).
- ⁹ P. Drude, ' *Theory of Optics*,' p. 364, 1913 edition.
- ¹⁰ Pannekoek, *Proc. Amsterdam Akad.*, **29**, 1165 (1926).
- ¹¹ J. N. Bhar, *Ind. Jour. Phys.*, **12**, 363 (1938).
- ¹² Dellinger, *Phys. Rev.*, **48**, 705 (1935).
- ¹³ Jonast, *La Meteorologic*, Jan.-Feb., p. 1 (1938).
- ¹⁴ M. N. Saha, *Proc. Nat. Inst. Sci. India*, **1**, 216 (1935); *Proc. Roy. Soc. A*, **160**, 195 (1937).
- ¹⁵ Worley and Jenkins, *Phys. Rev.*, **54**, 305 (1938).
- ¹⁶ Hopfield, *Phys. Rev.* **36**, 789 (1930).
- ¹⁷ S. K. Mitra and H. Rakshit, *Ind. Jour. Phys.*, **12**, 47 (1938).
- ¹⁸ R. C. Mazumdar, *Ind. Jour. Phys.*, **21**, 75 (1938).
- ¹⁹ S. P. Ghosh, *M.Sc. Thesis* (1938), Calcutta University
- ²⁰ D. F. Martyn and O. O. Palley, *Proc. Roy. Soc. A*, **154**, 455 (1936).